

Review

Studies on the Thermochemical Conversion of Waste Tyre Rubber—A Review

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Abstract: Waste from scrap tyres, due to its high volume (17 million Mg per year) and durability resulting from the physical and chemical properties, requires innovative approaches for efficient and environmentally friendly management. In many countries, the landfilling of waste tyres is banned (e.g., EU, USA, UK); however, waste tyres can be a source of valuable materials such as carbon black, pyrolysis oil, hydrogen-rich syngas, tyre char, as well as energy. The purpose of this article is to provide a synthesis of the state of knowledge regarding the thermal conversion of waste tyres by pyrolysis and gasification, taking into account the use of different measurement techniques and reactor types. These technologies are forward-looking and have a high degree of flexibility in terms of product sourcing, depending on the process conditions. The properties of waste from used tyres were analysed, i.e., the composition of the content of individual components and the main chemical substances. The results encompassed ultimate and proximate analyses of rubber from tyres, as well as the physical and chemical parameters of the tyre char obtained through pyrolysis. This article compiles available literature data regarding the impact of process and raw material parameters, such as temperature and time conditions, pressure, particle size, and catalyst addition on the pyrolysis and gasification processes. It also explores the influence of these factors on the yield and properties of the products, including pyrolysis oil, gas, synthesis gas, and tyre char.

Keywords: tyre waste; thermochemical conversion; pyrolysis; gasification



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1. Introduction

There is, today, increasing energy consumption resulting from the use of conventional fuels, due to, among other factors, a growing population, improving living standards in the sense of meeting material needs, dynamic industrialisation in the economies of developed and, especially, developing countries, as well as civilisation and urbanisation growth [1–4]. A huge challenge, therefore, is the search for alternative energy sources to meet energy needs while taking care of the environment [5]. An interesting alternative may be the possibility of using waste for the direct production of energy, but also fuels and chemical compounds, as it allows to use materials posing management challenges due to their quantity and nature [6,7]. One of the examples of this type of waste is used tyres; according to Ferdous et al. [8], some 17 million tonnes of such waste is generated each year, of which only 10% is recycled, and as much as 75% ends up in landfills (due to their characteristics and difficulty of disposal). Used tyres, compared to other waste, demonstrate high resistance to atmospheric conditions, i.e., humidity, temperature changes, or UV radiation, which makes this type of waste extremely difficult and cumbersome to manage safely and in an environmentally friendly manner. A consequence of the high stability of tyre waste is the long period of its degradation in the environment, which reaches up to 1000 years in the case of landfilling [9]. The result is a serious threat to health and the environment, as used tyres are a potential rainwater collection site, providing ideal breeding conditions for rodents and insects, including mosquitoes that can transmit

diseases potentially threatening to human health and even life, such as dengue fever and malaria [10]. Another risk from the landfilling of tyres is the risk of fires, which, according to Mohammad et al. [11], as a result of climate change, may occur with greater frequency, resulting in significant amounts of pollutants being emitted into the atmosphere, in addition to greenhouse gases [12]. The presence of water during tyre incineration can increase the generation of liquid products such as pyrolytic oil, as well as cause leaching problems with toxic metals and organic compounds, contributing to the poisoning of surrounding land, rivers and water intakes [10,13,14]. In turn, Page et al. [13] report that fine particles of waste tyres can account for between 28 and as much as 60% of the total microplastic contained in the marine environment. Hence, many countries are choosing to tighten policies regarding tyre waste management by introducing legislation to standardise the handling of this type of waste. For example, the European Union Parliament has banned member states from landfilling waste tyres, including those cut into smaller pieces [15].

Thus, every effort should be made to manage tyre waste with the utmost care for the environment along with the simultaneous benefits of allowing the recovery of main materials, generation of electricity and heat, and valuable chemical products. In the case of material recovery, the particular groups of materials from which the tyre was made are obtained, which will enable their reuse [16]. Energy recovery, on the other hand, involves subjecting used tyres to thermochemical transformations that enable the extraction of solid, liquid, and gaseous products to produce energy [17]. Note that thermochemical processes can also be directed towards the production of valuable products, i.e., fuels or chemicals. Thermochemical conversion processes, i.e., pyrolysis and gasification, can be used for such disposal of tyre waste. The pyrolysis process yields valuable products such as oil and gas. In addition, the by-product generated in a relatively large amount is char (up to 50%) [18,19], requiring further management. The gasification process can be used both to dispose of tyre char and tyre waste directly, and the resulting syngas can be used to generate electricity, chemical products, or fuels, or provide a source of hydrogen-rich gas [20]. Throughout the thermochemical conversion of rubber waste and the obtained products, the properties of the raw material, process conditions, technological factors, etc. will be crucial.

Given the above, the goal of the authors was to review the possibilities of the thermochemical conversion of rubber waste taking into account the above-mentioned factors. The paper presents the quantities and factors affecting the amount of waste tyres generated. The properties of waste tyres are analysed (i.e., the material characteristics of the tyres produced, as well as the physical and chemical properties of the tyre rubber and the resulting char from rubber produced via pyrolysis) and modern methods using material recycling are briefly discussed. The basic methods of the thermochemical conversion of waste tyres, i.e., combustion, pyrolysis, and gasification processes, are described, with particular emphasis on the influence of raw material and technological parameters on the course of these processes, as well as the yields of the products obtained.

2. Quantities and Properties of Waste Tyres

2.1. Vehicles, Tyres, and Tyre Waste

The intensive development of civilisation, society, and the economy is reflected in the increase in the number of vehicles on the roads globally. According to the International Organisation of Motor Vehicle Manufacturers [21], there were about 892 million motor vehicles on the road in 2005; by 2010, the number of vehicles had risen to a value of about 1055.7 million units, and by 2020 exceeded 1590 million units. In recent years, traditionally highly motorized Europe and North America have been joined by developing Asia and Oceania. The above was accompanied by a steady increase in vehicle production (Figure 1a) from a value of 58.4 million in 2000 to 97.3 million units in 2017, with subsequent years seeing a decline due mainly to the COVID-19 pandemic [22,23]. Data on the volume and production of motor vehicles contribute to an increasing demand for tyres. Figure 1b. shows the volume of tyre production in Europe from 2011 to 2020 (no detailed data for the

whole world), where an increasing trend can be observed with a decrease in 2020 caused by the COVID-19 pandemic. According to Markl and Lackner [24], the volume of global tyre production is estimated at about 40 million tonnes per year, so the European market accounts for about 12% of the total tyre production.

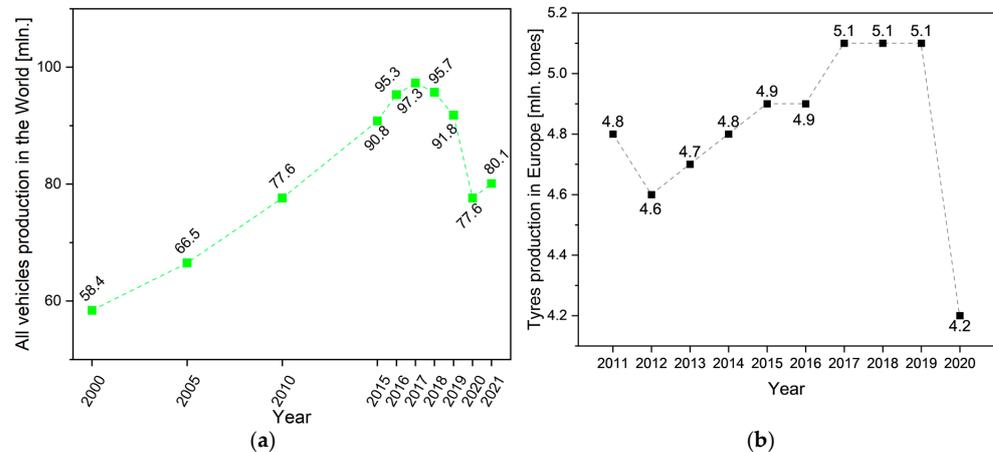


Figure 1. (a) Production vehicles in the world from 2000 to 2021; (b) European production of tyres from 2011 to 2020 (based on [25,26]).

The consequence of using such large volumes of vehicles and tyres is the generation of a huge number of used tyres and related waste, which should be rationally and efficiently disposed of to minimize their environmental impact. Approximately 1.5 billion used tyres are generated worldwide each year, which, converted to weight, is equivalent to about 17 million tonnes [8]. Moreover, it is predicted that by 2030, the number of used tyres could reach 4 to 5 billion units per year [27,28]. Globally, about 75% of waste tyres (12.75 million tonnes) end up in landfills, approximately 10% (1.70 million tonnes) are recycled, while the management of the remaining 15% (2.55 million tonnes) is unknown [8,29]. Analysing the different regions and countries of the world in terms of tyre consumption, it can be deduced that the countries of the European Union, the US, Japan, but also China and India are particularly responsible for generating about 88% of all used tyres [30]. Analysing the number of waste tyres generated in European countries (Figure 2), there is a clear and continuous increase from a value of 2.49 million tonnes in 2005 to 3.57 million tonnes in 2018 [31–33]. According to the European Tyre and Rubber Manufacturers' Association, in 2019, 55% (1.95 million tonnes) of the tyre waste generated was used for material recovery, 40% (1.43 million tonnes) was used for energy recovery, while the management of the remaining 5% (0.18 million tonnes) is unknown [32].

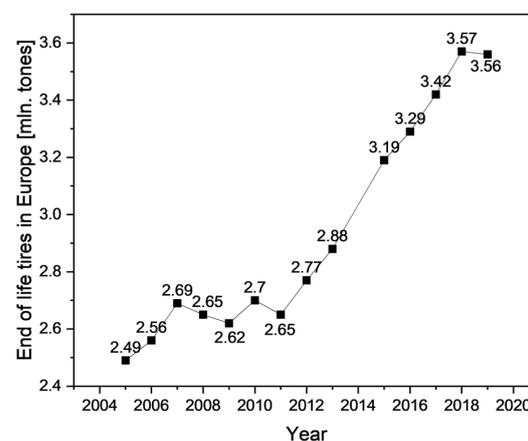


Figure 2. Amount of waste tyres in Europe from 2005 to 2019 (based on [31–33]).

2.2. Tyre Characteristics

Tyres are among the most essential components of a vehicle, the only part with direct contact with the road on which they travel, thus providing good traction [34]. Thus, they are key components for the safe and comfortable use of transportation for both drivers and passengers. Tyres used in motor vehicles should have certain properties to meet the requirements of various conditions and operating environments, including factors like shape, strength, vibration damping, heat dissipation, and electrostatic charge dissipation [35]. A tyre is a complex part of a vehicle, in which one can distinguish several structural elements made of different materials, including rubber, metals, or textiles that exhibit different properties. Thus, the final characteristics of a tyre are the product of the properties of the individual components from which the tyre is composed. To highlight the difference between different types of tyres, Table 1 collects data showing the material composition for different types of vehicles.

Table 1. Material composition of tyres depending on their intended use.

Type of Tyres	Rubber		Carbon Black	Silica	Metals	Textile	Others *
	Natural	Synthetic					
Car tyres [wt.%]							
[19]	14.0	27.0	28.0	-	14.0–15.0	-	-
[29]	22.0	23.0	28.0	-	13.0	-	14.0
[36] a	21.0–42.0	40.0–55.0	30.0–38.0	-	-	-	3.0–7.0
[36] b	41.0–48.0	-	22.0–28.0	-	13.0–16.0	-	4.0–6.0
[37]	21.2	24.5	18.9	7.7	10.8	3.7	13.1
[38]		47		22.5	14.0	5.5	11.0
Truck tyres [wt.%]							
[27]	27.0	14.0	28.0	-	14.0–15.0	-	16.0–17.0
[29]	30.0	15.0	20.0	-	25.0	-	10.0
[36]	41.0–45.0		20.0–28.0	-	20.0–27.0	-	0.0–10.0
[37]	37.1	10.0	22.3	1.3	21.1	0.2	8.0
[38]		45.0		21.0	23.5	1.0	9.5
Other tyres [wt.%]							
[27]		47.0		22.0	12.0	10.0	9.0
[39]		48.0		22.0	15.0	5.0	10.0
[40]		51.0		25.0	-	-	4.5

* Vulcanizing agents and additives.

The main materials from which a tyre is made, regardless of its purpose, are rubber compounds, metals, and textiles. The rubber compound is a composition of natural and synthetic rubber, carbon black and amorphous silica, vulcanizing agents, and also additives [29]. It can be seen from Table 1 that the rubber content varies from 40 to 50% regardless of the intended use of the tyre, with a slight predominance of synthetic rubber ~60% for passenger car tyres, while truck tyres have a predominance of natural rubber, which accounts for about 60 or even 80%. The most common varieties of synthetic rubber used in tyre production are butyl rubber and styrene-butadiene rubber [41]. The second key ingredient in the mix is a combination of carbon black and silica, whose function is to fill and strengthen the rubber structure, thus giving greater strength to the rubber [41,42]. Their content in tyres ranges from 20 to 30%. Based on the data presented by Valentini and Pegoretti [37], it can be noted that a higher silica content is observed in car tyres than in truck tyres. The next component included in tyres is metal, which is designed to strengthen the tyres mechanically [35,43–45]. For passenger cars, the content of the metal fraction ranges from 10–16%, while for trucks, a higher content of 14 to 27% of this material is used. Textiles are another group included in tyres, and their content ranges from a few to as much as 10%, with car tyres having a higher content. Among these materials, polyester or nylon are the most commonly used, and their purpose is to give strength to

the tyres [29,35,46]. The last group of materials used in the production of tyres is additives, the content of which is about 10%. These primarily include vulcanizing agents, softeners, and other additives that give the tyre distinctive properties [41]. Vulcanizing agents are the most important group of additives from the point of view of the tyre manufacturing process. Their action is based on the crosslinking and activation of polymer chains during the vulcanisation process. Thanks to these additives, the most important properties of the final product, such as flexibility, stiffness, and wear rate are shaped, so it becomes crucial to control the content of certain compounds, which include sulphur (including its compounds) and zinc oxide [29,47]. The second group of additives are softeners designed to support the preparation of a homogeneous mixture. These include phenylhydrazine salts, mercaptans, and natural oils including, for example, palm oil, and sunflower oil [48]. Other additives are designed to refine the final properties of tyres, especially in terms of their chemical strength. This group includes, among others, anti-ageing agents and protective agents against atmospheric conditions, including UV radiation, oxygen, or tyre temperature changes [48].

3. Disposal of Used Tyres

As shown above, a tyre is a complex structure of materials such as rubber, metals and textiles that are joined together in a homogeneous group, the properties of which determine the characteristics of the final product. Worn tyres have partially lost their original properties, especially mechanical ones, as a result of which it is impossible to continue operating them, primarily for safety reasons. Thanks to targeted legislative efforts, as well as the rapid development of research on waste tyre disposal, more and more alternatives to traditional tyre management are being developed. These methods, depending on their purpose, can be divided into:

- *Material recovery* is a process in which particular groups of materials from which the tyre was made are obtained so that they can be reused [16].
- *Energy recovery* is a process in which used tyre material undergoes thermochemical conversion, resulting in the extraction of fractions with applications aimed at energy production [17].

3.1. Material Recovery

Material recovery includes the mechanical processing of used tyres to separate individual materials, as well as shredding (Figure 3). Three main groups of materials are obtained, i.e., metal parts and textiles, which are reused, and shredded rubber waste, which is sent for further material recovery as well as energy recovery. The resulting rubber materials are a useful raw material that can be widely used as a filler or as an intermediate product with many applications. One of these applications is the use of waste rubber as an additive in the construction of asphalt road surfaces [49]. Studies conducted on the properties of asphalt binder mixtures with rubber particles indicate improvements in mechanical and performance properties, including an increase in the service life of the road surface, an increase in resistance to the formation of ruts on the road, resulting in lower maintenance and rehabilitation costs, as well as a reduction in noise from vehicle traffic [49–51]. Another example of the use of ground rubber from used tyres is as part of the aggregate required for concrete production [52]. Adequate tyre rubber content in the concrete mix results in an increase in its cyclic strength, better strength and impact resistance, increased ductility, and improved energy absorption capacity, while reducing drying shrinkage [52–54]. In addition, replacing some of the natural aggregates with ground rubber makes it possible to reduce the final density of the concrete, thereby effecting cost reductions [52]. Ground rubber from used tyres has also found its way into the production of paving blocks and flooring as a major component, and the final product is characterised primarily by increased resistance to environmental factors, resulting in extended service life, as well as improved plastic properties and higher impact resistance [16]. In addition, the addition of rubber from used tyres is widely used in many types of binders such as gypsum, epoxy resins,

bitumen, and plastic composites [53–55]. Finely ground rubber is also used as an infill for football fields with artificial turf and as one of the main ingredients in the production of basketball substrates, as well as athletic treadmills [56,57]. However, the polycyclic aromatic hydrocarbons, volatile organic hydrocarbons, heavy metals, plasticizers, and other additives present in the rubber particles that enhance the strength of the rubber can be leached by rainwater from the rubber structure and enter the groundwater, resulting in health risks [56]. Shredded tyres can also be used as an insulating layer under road surfaces, and as drainage material in solid waste landfills [58]. Shredded rubber material from used tyres can also be the main ingredient in the production of roofing materials, characterised by high resistance to weathering, especially in the event of hail, compared to conventional tiles or sheets [59].

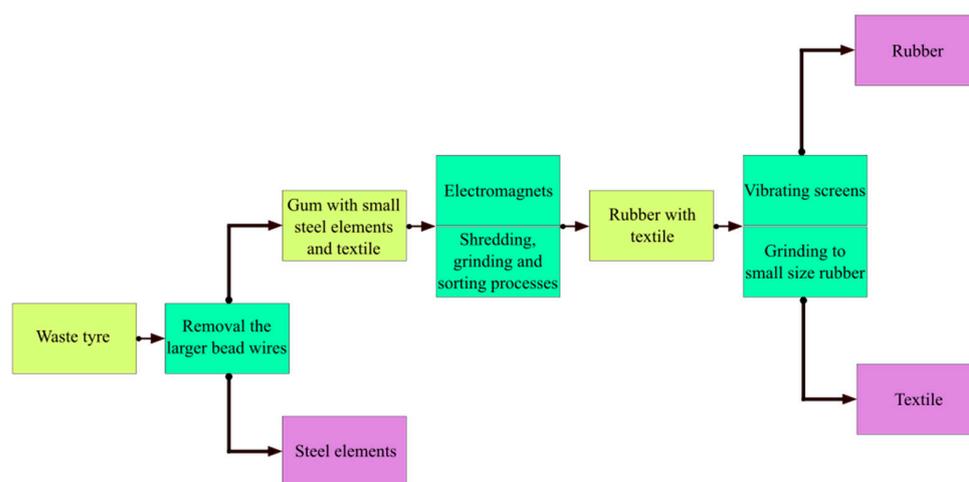


Figure 3. Schematic diagram of the material recovery steps of waste tyres [38].

One way to repurpose used tyres is to remanufacture them through retreading, which is the removal of the top worn layer of tread, the properties of which have deteriorated or been completely lost during use, and the application of a layer of new tread, thus restoring the original properties of the tyre. This type of tyre recycling is only possible if the tyre does not have any mechanical damage and structural defects; hence, it is limited to a relatively small amount of this type of waste [60]. Waste tyres have also found less frequent use as usable materials for retaining walls that are filled with soil or stones [61].

3.2. Energy Recovery

One way to manage the resulting rubber fraction from used tyres is through energy recovery, which involves thermal conversion of the waste using processes such as combustion, pyrolysis and gasification. The authors of this study particularly focus on thermochemical pyrolysis and gasification processes that enable the production of solid, liquid, and gaseous products that can be used in the production of heat or electricity, as well as chemicals and substitutes for certain fuels [62–65]. In order to present the energy potential and properties of used tyres, the ultimate and proximate analyses for various rubber materials are compiled in Table 2. In most of the works cited, the authors do not specify whether they are describing the characteristics of the rubber fraction itself or the used tyres, although judging by the results obtained (i.e., the ash content), it is mainly rubber material. In addition, individual parameters are given in different states (on a received, dry, and dry ash-free basis), which makes it difficult to analyse the data presented.

Table 2. Ultimate and proximate analysis results for various type of waste tyre.

Material	Ultimate Analysis [wt.%]					Proximate Analysis [wt.%]				Calorific Value [MJ/kg]
	C	H	N	S	O	FC	M	A	VM	HHV
Waste tyre [66]	74.8 ¹	5.5 ¹	0.7 ¹	1.1 ¹	9.0 ²	25.2 ²	1.2 ³	8.9 ³	64.8 ³	35.1 ³
Waste tyre [67]	85.9 ⁴	6.8 ⁴	0.7 ⁴	2.2 ⁴	4.5 ²	24.1 ²	2.3 ³	7.3 ³	66.3 ³	33.3 ³
Mixture of trucks, tractors, and cars tyres [68]	81.7 ³	6.5 ³	0.6 ³	1.9 ³	-	-	0.7 ³	6.6 ³	64.6 ³	-
Motorcycle tyre [69]	75.5 ¹	6.8 ¹	0.8 ¹	1.4 ¹	15.5 ²	20.9 ³	1.5 ³	20.1 ³	57.5 ³	29.1 ¹
Waste tyre [70]	82.1 ¹	7.6 ¹	0.6 ¹	2.1 ¹	7.5 ¹	33.4 ¹	0.9 ¹	5.2 ¹	60.6 ¹	-
Waste tyre [71]	73.8 ¹	6.8 ¹	0.3 ¹	1.3 ¹	9.0 ¹	23.2	1.0	8.8 ¹	68.0	36.0 ¹
Car tyre [72]	78.3	7.1	0.8	-	13.8 ²	30.5 ¹	1.5	4.3 ¹	61.6 ¹	30.2 ¹
Waste tyre [73]	79.5 ¹	9.2 ¹	0.6 ¹	2.0 ¹	8.7 ¹	33.1 ¹	1.2 ¹	3.2 ¹	62.5 ¹	-
Waste tyre [74]	80.4	8.7	0.3	1.6	9.0 ²	23.5 ¹	1.0 ¹	5.5 ¹	69.1 ¹	38.3 ¹
Waste tyre [75]	84.1 ¹	7.3 ¹	0.3 ¹	2.3 ¹	0.8 ²	33.5 ¹	0.8	5.2 ¹	61.3 ¹	38.6

¹—dry basis, ²—by difference, ³—as-received basis, ⁴—dry ash-free basis.

The rubber materials analysed had an elemental carbon content of about 80%, comparable to highly metamorphosed hard coals [71]. In addition, they had a relatively high hydrogen content. Such an elemental content of C and H translates into a high calorific value of these materials, i.e., the higher heating value is in the range of 29.1–38.6 MJ/kg (note the different states given by the cited authors). These features confirm the high energy potential of used tyres [72]. In addition, low moisture content and, for most samples, ash content can be observed, which, in addition to having a favourable effect on calorific value, makes it possible to use rubber waste in thermochemical processes, reducing, if any, operational problems associated with corrosion [73]. Also noteworthy is the high content of volatile matter in used tyres, indicating a high potential for the formation of liquid and gaseous fractions [74,75]. In turn, the value of the fixed carbon, combined with the ash content, makes it possible to estimate the amount of the solid product—tyre char (up to 50%) formed during the pyrolysis process. It is noteworthy that the varying oxygen content (from 0.8 to as much as 15.5%) can affect the reactivity of rubber waste, including in catalytic processes, especially with alkali metals and alkaline earth metals, through the formation of active sites for interaction with oxygen-containing functional groups like -OH and -COOH [76]. The unfavourable sulphur content of tyres varies from 1.1 to 2.3% and comes mainly from vulcanisation additives [29,47].

3.3. Combustion of Waste Tyres

Combustion is the simplest of all the processing methods for carbon materials based on thermal conversion to produce energy. Due to its elemental composition and potential calorific value, rubber from used tyres is an excellent raw material for this process, allowing significant amounts of energy to be obtained. Li et al. [77], conducting thermogravimetric studies on the combustion of waste tyres, showed that the process consists of five stages. The first three stages obtained on the DTG curve (Figure 4) show the release and oxidation of volatile compounds at temperatures of 250–350 °C, 360–420 °C, and 420–480 °C. The mass loss during these three stages is about 42% of the total mass. The next two stages, occurring in the temperature ranges of 520–600 °C and 650–800 °C, respectively, are related to the afterburning of the char. At the same time, much research is focused on the possibility of co-combusting rubber waste with other fuels. Li et al. [77] note that when co-combusting tyre rubber and coal with high ash content, the ignition temperature decreases as the proportion of rubber in the burned mixture increases, and there is also an increase in the maximum

combustion rate. Pan et al. [78] also note that the addition of tyre rubber improves ignition characteristics, lowers the final temperature of the process, and lowers the value of the activation energy. Also, Wu et al. [79] demonstrated, in their analysis, the possibility of co-combustion of rubber waste with coal, obtaining a lower ignition temperature of the mixtures, which affects the stabilisation of the flame in boilers. Singh et al. [80] on the other hand, proved that the presence of tyre rubber can contribute to an 80% reduction in NO compared to burning conventional carbon fuels. Carmo-Calado et al. [81] investigated the possibility of the co-combustion of rubber from used tyres and miscanthus in ratios of 0:1, 1:4, 2:3, and 3:2. The authors show an increase in generated power corresponding to an increase in the amount of rubber fraction, progressing from a value of 100 kW for miscanthus alone to 156.9 kW for the mixture with the highest proportion of rubber. At the same time, the authors point out the problems of fuel feeding and slag removal when there is a high content of rubber fraction in the mixture. Gieré et al. [82] showed that the addition of 5 wt.% of tyre rubber during coal combustion results in an increase in metal emissions, especially Zn and HCl, with a parallel slight decrease in carbon monoxide concentration. Singh et al. [83], while studying the behaviour of ZnO/Zn during the combustion of tyre rubber, suggested that above 1200 °C, ZnO transitions to the gas phase, while Zn forms a submicron aerosol. A study by Zhang et al. [84] confirms that the zinc contained in the rubber waste is volatilised during combustion; however, the authors note that a large amount of Zn is bound in the ash. On the other hand, when studying the co-combustion of char from waste tyres and lignite, Onenc et al. [85] indicated a reduction in the reactivity of the mixture through an increase in the ignition temperature compared to burning only coal. In addition, it should be remembered that due to the chemically complex structure of tyre rubber, its combustion carries potential environmental risks, from the emission of toxic compounds, including carbon monoxide, sulphur oxides, or volatile organic compounds [67]. Mentés et al. [86] noted that the amount of polycyclic aromatic hydrocarbons in the solid phase deposited on the filter during tyre combustion exceeds the concentrations considered acceptable in some European countries (at 0.005 mg/m³), regardless of the temperature conditions.

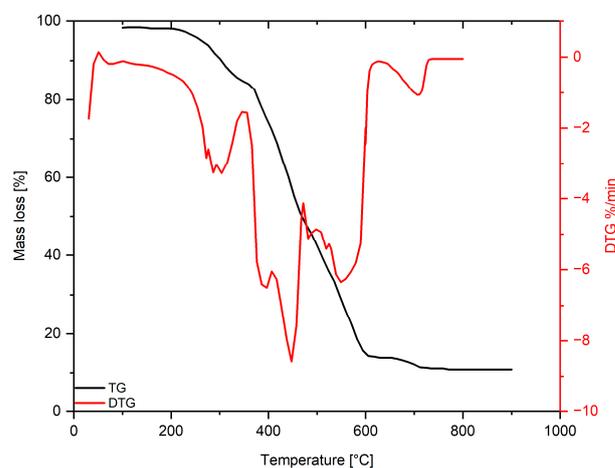


Figure 4. DTG and TG curves of the combustion of waste tyres [77].

In summary, co-combustion with the addition of waste rubber from tyres yields the following results: (i) for biomass, it improves the stability of the fuel mixture and increases the obtained power; (ii) for coals, the reactivity of the fuel, stability and intensity of the process increases; (iii) the addition of tyre char reduces the reactivity of the mixture; (iv) it is associated with operational problems (fuel feeding and slag removal) and increased emissions of sulphur oxides, metals (Zn), or organic compounds (including PAHs).

The other two thermal conversion processes for tyre waste, i.e., pyrolysis and gasification, will be described in more detail in the following sections.

4. Pyrolysis of Waste Tyres

Pyrolysis is one of the most promising thermochemical conversion processes for managing difficult wastes, resulting in a wide range of useful gaseous, liquid, and solid products with great potential for energy production, as well as the synthesis of chemicals and alternative fuels [62–65]. The inert atmosphere and the relatively low temperature in the reactors used in tyre pyrolysis, compared to boilers operated in conventional combustion processes, translates into a reduction in pollutants such as compounds with oxidised structures (alcohols, organic acids, furans, or some amides) [29,67,87]. Due to its high energy potential and high elemental carbon content, rubber from used tyres could be an attractive raw material for this technology. Table 3 compiles the results of a literature review on studies on the pyrolysis process of waste tyres, along with a characterisation of the most important process and technological conditions (measurement conditions, heating rate, type of reactor) and raw materials (particle size, presence of catalyst), as well as the percentage yield of the obtained gas, liquid, and solid fractions. The examinations were conducted in different types of reactors, i.e., fixed bed, semi-batch, and batch reactors, as well as rotary reactors, and the following is an analysis of the data, presented in Table 3.

Table 3. Description of the most important parameters during the pyrolysis of waste tyres.

Material [Reference]	Reactor	Catalyst	Particle Size [mm]	Measurement Conditions			Yields [%]		
				Temperature [°C]	Pressure	Heat. Rate [°C/min]	Gas	Liquid	Solid
Waste tyre [88]	Fixed bed	-	1–2	500	atmospheric	10	22.6	38.3	36.7
				600			28.7	30.9	36.6
				700			29.5	30.5	37.1
				800			30.1	29.8	36.9
Light vehicle tyre				550			12.5	43.0	44.5
				600			12.0	45.0	43.0
				650			10.0	51.0	39.0
				700			12.5	48.5	39.0
Medium vehicle tyre	Batch reactor	-	10–30	650	3 bars	20	17.5	44.0	38.5
				700			16.5	41.0	42.5
				750			12.5	45.0	42.5
				800			11.0	45.0	44.0
Heavy vehicle tyre [89]				650			12.5	54.0	33.5
				700			9.5	58.0	32.5
				750			10.0	64.0	26.0
				800			9.5	58.0	32.5
Waste tyre and blast-furnace slag [63]	Rotary pyrolysis reactor	-	0–10	600	atmospheric	-	7.1	30.2	62.7
							8.6	32.7	58.7
							8.1	39.1	52.8
							8.0	40.7	51.3
							9.3	31.1	59.6
							8.8	34.9	56.3
				800			8.2	40.0	51.8
							8.8	45.7	45.5
							8.3	47.2	44.5
							10.1	53.7	36.2
							10.5	55.8	33.7
							11.1	57.3	31.6
[90]	Fixed bed	-	0.15–0.3	800	atmospheric	20	17.0	36.0	47.0
							14.0	47.5	38.5
							16.0	44.0	40.0
							18.0	39.5	42.5
							17.5	38.0	44.5
							28.5	43.0	28.5
							22.5	45.0	32.5
							21.0	41.5	37.5
							18.0	38.5	43.5
							27.5	51.0	21.5
							22.0	51.5	26.5
							20.0	41.5	38.5
							19.5	39.0	41.5

Table 3. Cont.

Material [Reference]	Reactor	Catalyst	Particle Size [mm]	Measurement Conditions			Yields [%]		
				Temperature [°C]	Pressure	Heat. Rate [°C/min]	Gas	Liquid	Solid
Light vehicle tyre Case I	Batch reactor	-	2 × 3	550	atmospheric	8–11	19.0	36.0	45.0
		CaCO ₃					23.0	39.5	37.5
		Al ₂ O ₃					30.0	32.0	38.0
		ZSM-5					25.5	30.0	44.5
		MgO					17.0	42.5	40.5
		-					19.0	36.0	45.0
Light vehicle tyre Case II [91]	-	CaCO ₃	-	550	-	-	37.0	22.5	40.5
		Al ₂ O ₃					33.0	26.0	41.0
		ZSM-5					25.0	34.5	40.5
		MgO					20.0	38.5	41.5
		-					41.0	25.5	33.5
Waste tyre [92]	Semi-batch reactor	-	2–3	500	-	-	40.0	24.5	35.5
		Biochar					15.4	32.9	51.7
Waste tyre [65]	-	Na ₂ CO ₃	-	450	Vacuum (3.5–4.0 kPa)	20	21.8	42.1	36.1
				500			16.0	47.1	36.9
				550			16.3	48.8	34.8
				600			14.8	36.5	48.7
				450			15.3	42.0	42.7
				500			14.6	47.8	37.6
		NaOH		600			16.2	48.5	35.2
				450			14.2	38.5	47.0
				480			13.7	49.7	36.7
				500			13.3	48.1	38.6
				520			16.8	46.9	36.4
				550			20.8	39.0	40.2

4.1. Effect of Temperature and Heating Rate

One of the most important factors that influences the characteristics of the products obtained when conducting the pyrolysis process is the set of process conditions. Temperature and heating rate are factors that determine the shares of each product and the efficiency of the entire process. As the final temperature increases, there is an increase in the yield of light hydrocarbon compounds, resulting in an increase in the proportions of the liquid fraction and the gas fraction at the expense of the resulting tyre char [93]. According to Choi et al. [88], an increase in temperature from 500 to 800 °C during the pyrolysis of used tyres results in an increase in the share of the gas fraction from 22.6 to 30.1 wt.% at the expense of a decrease in the share of the liquid fraction from 38.3 to 29.8 wt.%, while the yield of the solid fraction does not change significantly, amounting to about 37 wt.%. Luo and Feng [63], on the other hand, observed a decrease in the yield of the solid fraction from 50.4% at 600 °C to 31.43% at 1000 °C, and an increase in the yield of the liquid fraction from 41.4 to 58.3%, and the gas fraction from 8.2 to 10.3% for the same temperature values. Singh et al. [89] showed a decrease in solid product yield with increasing temperature for a tyre from a light vehicle, ranging from about 44.5 to 39%, and for a tyre from a heavy vehicle, ranging from 33.5 to 26%, while there was no significant change in the yield of this fraction for tyres from a medium-weight vehicle. For the liquid fraction, on the other hand, there is an increase in yield with increasing temperature for tyres from a light vehicle, ranging from about 43 to 51%, and for tyres from a heavy vehicle, ranging from about 54 to 64%. As with the solid fraction, no clear effect of temperature is observed for the yields of the liquid fraction obtained from tyres from a medium-weight vehicle. In the case of gas products, there is a decline in their shares regardless of the type of tyre.

The studies also show a significant effect of heating rate on product characteristics and yields. Slow heating determines the longer residence time of rubber particles in the reactors while leading to the promotion of secondary reactions between solid and volatile compounds, resulting in lower shares of the liquid fraction and higher shares of the solid and gas fractions. For higher heating rates, the residence time of rubber particles in the reactor is reduced, resulting in higher yields of liquid components [94]. Mkhize et al. [95] showed that an increase in the heating rate from 0.86 to 15 °C/min to a temperature of 450 °C leads to a decrease in the gas fraction shares from 23.1 to 19.7 wt.% and an increase in the liquid product yields from 39.6 to 43.7 wt.%. At the same time, the authors did not

observe a clear effect of the heating rate on the shares of the solid fraction, the shares of which were about 37 wt.% in both cases.

4.2. Effect of Particle Size

Particle size is a parameter that affects the kinetics of the process and the intrinsic nature of heat transfer [96]. Oyedun et al. [97] note that particle size has significant effects during slow pyrolysis since a low heating rate implies a significant heat transfer resistance, which is higher the larger the particle size. The upshot is that for larger particle sizes, the mass loss curves are shifted toward higher temperatures [98]. In addition, Oyedun et al. [97] indicate that the pyrolysis time for rubber from smaller-sized tyres is shorter and the amount of energy delivered is greater than for larger-sized particles. Hence, parameters such as heating rate, particle size, and reaction time must be adjusted to ensure efficient and economically viable conversion.

4.3. Effect of Pressure

The effect of total pressure is not thought to be as significant as temperature or heating rate [94]. However, Zhang et al. [65] point to some advantages of conducting the pyrolysis process under vacuum conditions, which include a shorter residence time in the reactor, limiting secondary reactions, a higher yield of pyrolysis oil, and the generation of a group of aromatic compounds. Such a relationship is confirmed by data compiled by Ma et al. [99] for an increase in total pressure from 0.1 to 1.5 MPa, resulting in a decrease in liquid fraction shares from 45 to 32 wt.%. The authors note that, as the total pressure increases, the content of olefin fractions in particular increases, and the content of alkanes and C₇₊ cyclic aromatic hydrocarbons decrease.

4.4. Effect of Catalysts

The addition of catalysts to the pyrolysis of waste tyres can affect both the rate and efficiency of the process and the composition of the resulting products. Zhang et al. [65] studied the effect of sodium carbonate and sodium hydroxide during the pyrolysis of used tyres in the temperature range of 450–600 °C, and the presence of these catalysts resulted in an increase in the share of the liquid fraction from 32.9 wt.% for the tyre alone, to 36.5 wt.% and 38.5 wt.% with the addition of Na₂CO₃ and NaOH, respectively. At the same time, a decrease in the yield of tyre char is observed, from 51.7 wt.% obtained for the tyre alone, to 48.7 wt.% in the case of Na₂CO₃ and 47.0 wt.% in the presence of NaOH. Kordoghli et al. [91] pyrolysed used tyres in the presence of CaCO₃, Al₂O₃, ZSM-5, MgO catalysts at 550 °C. The presence of these compounds (especially CaCO₃) promotes an increase in the share of gaseous products (from values of 19.0 wt.% to 37.0 wt.%). In addition, calcium carbonate allows the highest reduction in liquid and solid fraction yields, to 22.5 wt.% and 37.5 wt.%, respectively. Niu et al. [90] pyrolysed tyre mixtures with biomass derived from rice husks, wheat straw, and bamboo stalks. The increase in tyre rubber in the mixture with wheat straw and bamboo stalks promotes a reduction in the liquid fraction, as well as the gas fraction. In the case of char, the addition of tyre causes an increase in the shares of this fraction for all the mixtures analysed. Chao et al. [92] pyrolysed rubber from used tyres in the presence of a biomass-derived biocarbon catalyst. The obtained results show that the catalytic addition does not significantly affect the obtained products, since the difference in yield between the catalytic and non-catalytic processes for liquid and gaseous products is 1 wt.%, while for the solid product, it is 2 wt.%.

4.5. Characteristics of Pyrolytic Gas

Analysing the yields of the various products of tyre waste pyrolysis, compiled in Table 3, it can be seen that the proportion of the gas fraction, regardless of the conditions for conducting this process, falls within fairly wide limits, from a dozen (~10%) to about 20% and even 40%, and its calorific value can be as high as 42 MJ/kg [100]. Tyre pyrolysis gas has a significant hydrogen content, which increases with increasing temperature [63,65].

According to Zhang et al. [65], at 600 °C, the H₂ content can be as high as 60%. Other components included in the gaseous fraction are carbon monoxide and carbon dioxide, whose content varies from a few to about 30% [63,65]. Unlike hydrogen, the concentration of CO and CO₂ in the reaction gas decreases as the temperature increases. The gas also includes light hydrocarbons (CH₄, C₂H_n and C₃H_n), and their concentration varies around 10% [63]. In addition, as with carbon oxides, for light hydrocarbons, their content decreases due to the increase in temperature [65]. Small contents of sulphur compounds (H₂S, COS, CS₂), as well as nitrogen (NH₃, NO₂), may occur in the pyrolytic gas, but their content should not exceed a few percent [29]. As mentioned in an earlier section, the yield of each gas component is affected by many processes, technological and feedstock factors, so its composition can vary. Pyrolysis gas is mainly used to meet energy needs during the pyrolysis process [29].

4.6. Characteristics of Pyrolytic Oil

The liquid fraction obtained during the pyrolysis of waste tyres is a complex mixture of hydrocarbons with a calorific value of about 40 MJ/kg [29,101]. The share of liquid products, as in the case of gas, is strongly dependent on the conditions of conducting the conversion of the raw material and varies from 30 to 50%. As indicated by the liquid phase analyses performed by Kumar et al. [101,102] and Wang et al. [103], the main components are aromatic and aliphatic hydrocarbons, nitrogen compounds, phenols, organic acids, aldehydes, ketones, esters, furans, or polycyclic aromatic hydrocarbons. The resulting oil can be used as a potential fuel substitute, for which its calorific value and sulphur content should be measured [29,104]. In addition, pyrolytic oil can be used as a potential source of many important chemicals, such as benzene, toluene, xylene, and limonene, which are used in the production of pigments, dyes, synthetic plastics, fibres, resins, or adhesives [29].

4.7. Characteristics of Tyre Char

The final product resulting from the pyrolysis of used tyres is the solid phase or tyre char. The share of this fraction can range from 30 to as much as 50% and strongly depends on the process conditions of pyrolysis, especially the temperature [63,65,88–92]. Like gaseous and liquid products, tyre char also has significant energy potential, as its calorific value is about 30 MJ/kg, being similar to highly metamorphosed hard coals or anthracite [105,106]. The compiled results of the ultimate and proximate analysis of selected waste tyre chars (Table 4) show that this product consists primarily of elemental carbon, as its content for most of the cases considered ranges from 80 to 85% [88,107,108]. Also observed is a significant sulphur content of ~2–5%, derived from vulcanisation compounds, which largely remain in the solid fraction during pyrolysis [29,47]. The total hydrogen and nitrogen content usually does not exceed 2% [88,107,108]. Similarly, the moisture content and volatile matter content usually remain very low, at no more than 4% for moisture and 8% for volatile matter content, which are strongly dependent on the final pyrolysis temperature [109]. The ash content of tyre char varies from a dozen to as much as 20% [108–110].

Table 5 provides a summary of the morphological properties of tyre pyrolysis char, which are relevant to the reactivity of this material [109], as well as its sorption properties. Values of specific surface area ranging from 70 to 150 m²/g suggest that this parameter depends on the temperature conditions during the reactor operation, as well as the type of reactor. According to [88,107], there is an optimal temperature for which the specific surface area takes the highest value, below or above which its value decreases. The pore volumes of tyre char are about 0.2–0.4 m³/g, with the largest proportion observed for mesopores with diameters ranging from 10 to 25 nm. The compiled results on the surface structure of tyre char are similar to some commercial carbon materials, thus allowing them to be used as a replacement for carbon fillers in the rubber industry [109].

Table 4. Ultimate and proximate analysis of char from used tyres.

Reference	Conditions	Ultimate Analysis [wt.%]					Proximate Analysis [wt.%]				
		C	H	N	S	O	FC	M	A	VM	
[108]	9 W/g ⁴	82.3	0.5	0.5	3.0	-	82.1	0.1	16.3	1.5	
	15 W/g ⁴	82.7	0.4	0.4	2.9	-	82.7	0.1	16.1	1.1	
	24 W/g ⁴	83.2	0.4	0.4	3.1	-	82.6	0.1	16.3	1.1	
[88]	500 °C	82.8	0.6	0.4	4.0	-	-	-	12.2	-	
	600 °C	83.0	0.4	0.4	4.5	-	-	-	11.7	-	
	700 °C	86.2	0.4	0.2	1.7	-	-	-	11.5	-	
	800 °C	85.6	0.3	0.2	2.0	-	-	-	11.9	-	
[107]	400 °C	80.3	2.1	0.3	2.4	7.7 ¹	-	-	7.3	-	
	500 °C	81.2	2.0	0.2	1.7	5.9 ¹	-	-	9.0	-	
	600 °C	81.3	1.8	0.2	2.3	4.2 ¹	-	-	10.3	-	
	700 °C	83.5	1.6	0.3	2.5	1.8 ¹	-	-	10.3	-	
	800 °C	83.3	1.0	0.2	2.5	0.1 ¹	-	-	13.0	-	
	900 °C	88.0	1.0	0.2	2.6	0.1 ¹	-	-	8.0	-	
[111]	500 °C	74.6	1.1	0.5	2.5	-	-	-	-	-	
[112]	850 °C Fixed bed	77.4 ²	0.4 ²	0.4 ²	2.3 ²	3.1 ²	-	-	17.2 ²	-	
	850 °C Rotary oven	73.9 ²	0.4 ²	0.4 ²	2.5 ²	3.5 ²	-	-	20.4 ²	-	
[110]	700 °C	84.4 ³	1.3 ³	0.5 ³	2.3 ³	-	79.3 ³	3.6 ³	12.4 ³	4.7 ³	
[109]	400 °C	85.3	0.3	4.3	-	-	83.2	0.7	7.7	7.8	
	450 °C	90.6	0.6	0.4	-	-	88.8	0.5	7.0	3.8	
	500 °C	88.8	0.6	0.5	-	-	87.6	1.0	6.5	4.9	
	550 °C	89.2	0.5	0.4	-	-	88.2	0.7	6.7	4.4	
	600 °C	89.1	0.5	0.4	-	-	88.9	0.5	6.8	3.7	

¹—by difference, ²—dry basis, ³—as received, ⁴—W/g—specific microwave power per gram.

Table 5. Physical properties of char from used tyres.

Reference	Conditions	S _{BET} [m ² /g]	V _{micropore} [cm ³ /g]	V _{mesopore} [cm ³ /g]	V _{macropore} [cm ³ /g]	V _{total} [cm ³ /g]	Average Pore Diameter [nm]
[88]	500 °C	73.47	0.0022	0.1829	0.0110	0.1961	10.67
	600 °C	77.63	0.0047	0.1806	0.0092	0.1945	10.02
	700 °C	71.55	-	0.3505	0.0167	0.3672	20.53
	800 °C	70.87	-	0.3645	0.0776	0.4421	24.95
[107]	400 °C	10.0	0.000	0.023	-	0.023	-
	500 °C	156.0	0.024	0.099	-	0.123	-
	600 °C	136.0	0.015	0.178	-	0.193	-
	700 °C	96.0	0.013	0.174	-	0.187	-
	800 °C	85.0	0.008	0.192	-	0.200	-
	900 °C	87.0	0.008	0.104	-	0.112	-
[109]	500 °C	44.7	-	-	-	0.17	14.96
[111]	500 °C	70.0	-	-	-	0.39	22.97
[112]	850 °C Fixed bed	57.0	0.02	0.23	-	0.25	-
	850 °C Rotary oven	68.0	0.02	0.25	-	0.27	-
[113]	900 °C	38.0	-	-	-	-	-

5. Waste Tyre Rubber Gasification

The gasification process is a thermochemical conversion using a gasification agent, i.e., steam, carbon dioxide, air, oxygen, hydrogen, and their mixtures [114], which, depending on, among other factors, the technological solution, the conditions of the process and the type of raw material, can be directed towards the production of differentiated products (fuels, chemicals, or energy). The basic product of the process is syngas, the most important components of which are primarily hydrogen and carbon monoxide, as well as carbon dioxide, methane, and light hydrocarbons. Due to the course of gasification and the characteristics of the products obtained, this process is included not only in the group of energy recovery methods (combustion of syngas and generation of heat and electricity), but also in material recovery, since syngas can be used to synthesize substitutes for conventional fuels, but also chemical substances [115]. Since gasification is one of the well-understood, dynamically developed technologies with high utility potential, it can replace conventional waste processing methods such as landfilling or combustion, as it allows the use of a wide range of raw materials with diverse characteristics while producing value-added products [114].

Many reports can be found in the literature regarding studies on the gasification of both the rubber fraction from used tyres and the tyre char and oil from their pyrolysis process. The aforementioned potential feedstocks are attractive materials for the gasification process due to their high energy value, as well as their elemental composition (Tables 2 and 4, respectively). Table 6 compiles publications on the gasification and activation of waste tyres, as well as co-gasification with other materials, including catalysts. It presents the type of reactor, the raw material used (used tyres, tyre char and oil derived from pyrolysis) and its particle size, the process conditions (temperature and pressure), and the gasification agent, as well as a brief description of the research conducted. The gasification examinations were conducted under various conditions (temperature ranging from 350 to 1700 °C, pressure up to 45 MPa, particle size up to 30 mm) in different types of reactors, i.e., fluidized and fixed bed, tubular, batch, plasma, as well as rotary reactors, and using gasification agents such as air or oxygen, steam, CO₂, and their mixtures.

Table 6. Study on the gasification of used tyres and tyre char.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[116]	Fluidized bed	Tyre powder	0.4–2.1	350–900	-	Air	Evaluation of the effects of different process conditions (air amount and temperature) and raw materials (feeding and particle size) on the parameters characterising the gasification process and the obtained products.
[117]	Rotary furnace	Tyre char	≤0.15	925–1100	-	CO ₂ , steam	Effects of temperature and type of gasification agent on the structure of pyrolysis tyre char during its activation.
[118]	Fluidized bed	Chars of tyre, sewage sludge, rietspruit, activated carbon	0.355–0.710	800–1000	-	CO ₂	Comparison of reactivity of tyre char and char from other materials.
[119]	Thermobalance	Chars of tyre, sewage sludge, and coal	-	550–850	-	Steam	Analysis of the kinetics of the gasification process of various chars, including char from tyre pyrolysis.
[120]	-	Tyre char	-	750–900	-	CO ₂ , steam	Effects of temperature, activation time, and type of activation agent on the morphological properties of tyre char.

Table 6. Cont.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[121]	Fluidized bed	Waste tyre scrap, sewage sludge	0.6–1.2	650–850	-	Steam	Analysis of the possibility of co-gasification of used tyres with sewage sludge.
[122]	Fluidized bed	Waste tyre	–	400–800	-	Air	Analysis of the effect of temperature and air amount on the yields of gaseous and solid products.
[123]	Fixed bed	Tyre char	–	800–900	-	CO ₂	Analysis of the effect of temperature, flow rate of the activating agent, and reaction time on the properties characterising the surface of the obtained solid product.
[124]	Rotary kiln reactor	Scrap tyre, RDF, poplar	–	850	0.1	Steam	Evaluation of steam gasification of various raw materials, including used tyres, along with a characterisation of the resulting gas products.
[125]	Fixed bed	Tyre char	≤1	850–900	0.12	Steam	Effect of temperature during steam activation of low-reactive tyre char.
[126]	Moving bed	Waste tyre char, lignite char	0.2	850	2.7	Steam–oxygen	Evaluation of the possibility of co-gasification of lignite and used tyres—qualitative analysis of the gas obtained and the parameters determining the course of the process.
[127]	Rotary kiln gasifier	Rubber tyre	–	850	-	Steam	Analysis of the effect of gasification agent concentration on gas fraction yield.
[128]	TGA	Scrap tyre, sewage sludge, industrial sludge, fluff	0.1–30	1250	0.1	Steam	Thermogravimetric gasification of various materials, including rubber from used tyres.
[129]	Fluidized bed	Scrap tyre	0.6–1.0	720–820	-	Steam, air–steam, air–CO ₂	Effect of the type of gasification agent on the calorific value and composition of the gas obtained.
[130]	Fixed bed	Distillation scrap tyre char, semianthracite, medium and high-volatile bituminous coal	0.1–0.2	1000	0.1–1.5	Steam-oxygen	Analysis of the effect of pressure on the gasification of various materials and the composition of the resulting gas products.
[131]	Rotary kiln reactor	Waste tyre	≤6	850–1000	0.1	Steam	Analysis of the effect of the temperature of the tyre rubber gasification process on the characteristics of the obtained products.
[132]	Fixed bed	Tread rubber–Ni–Mg–Al	–	800	-	Steam	Gas product yields during a two-step pyrolysis/gasification reaction of tyre rubber tread in the presence of a Ni–Mg–Al catalyst.

Table 6. Cont.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[133]	Fixed bed	Rubber tread-Ni/CeO ₂ /Al ₂ O ₃	≤6	800	-	Steam	Effect of the presence and amount of catalyst on yields and composition of gas products during two-stage pyrolysis–gasification of tyre rubber.
[134]	Rotary kiln reactor	Scrap tyre–olivine, dolomite	≤2		0.1	Steam	Effects of the presence of two types of catalysts on gas product yields and gas composition from the gasification/reforming of used tyres.
[135]	Fixed bed	Rubber tread-Ni/Al ₂ O ₃	≤6	600–900		Steam	Effects of the presence and amount of catalytic additive, process temperature, and amount of steam on product yields and gas composition during a two-step pyrolysis/gasification reaction of tyre tread.
[136]	-	Tyre char, palm empty fruit bunch, almond shell	≤0.075	850–1000	-	CO ₂	Analysis of the gasification reaction course of tyre char with the addition of two types of biomass chars as potential catalysts.
[137]	Fixed bed	Tread rubber-Ni/Al ₂ O ₃ , Ni/dolomite		800		Steam	Effect of the addition of two catalysts on the yield of gaseous products during the two-stage pyrolysis–gasification process of tyre rubber.
[138]	-	Tyre char, coal chars	≤0.075	900–975	0.1	CO ₂	Comparison of the gasification course, reactivity, and kinetic parameters of chars from tyre and coal pyrolysis, as well as their blends.
[30]	TGA	Scrap tyre	0.5–10	1000	-	Steam	Thermogravimetric study of the gasification process of rubber from car and truck tyres of different particle sizes.
[139]	Fixed bed	Tyre char, wood pellets	≤1	700–900	-	Steam	Possibilities of using tyre char to remove tar from biomass pyrolysis during steam gasification.
[140]	-	Tyre char, coal chars	0.063–0.105	1000–1300	-	CO ₂	Comparison of reactivity and gasification kinetics of chars from pyrolysis of tyre and coal.
[141]	-	Tyre char, cattle manure, palm empty fruit bunch, almond shell, rubber seed shell	0.150–0.212	1127	-	CO ₂	Effect of heating rate and addition of biomass as potential sources of catalytic compounds on the characteristics and kinetics of the gasification process of tyre char.
[142]	Tubular batch reactor	Scrap tyre-Ba(OH) ₂ , Ca(OH) ₂ , Mg(OH) ₂ , Ni/SiO ₂ -Al ₂ O ₃ , Ru/Al ₂ O ₃	-	325–625	21–23	Subcritical and supercritical steam	Analysis of the effect of process parameters and the presence of different types of catalysts on the gasification of used tyres under subcritical and supercritical conditions.

Table 6. Cont.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[74]	Fixed bed	Waste tyre	0.5–1.0	600–800	Atmospheric	Air, oxygen	Analysis of the effect of flow rate and type of gasification agent on product yields, when gasifying rubber from tyres.
[143]	Fixed bed	Rubber tread	20 × 20	700–1000	Atmospheric	CO ₂	Effect of temperature on the yield of gas products and the quality of the obtained syngas.
[144]	Fixed bed	Tyre char	–	750–1050	Atmospheric	CO ₂	Effect of gasification agent concentration, reaction time on conversion rate and kinetic parameters using several models during gasification/activation of tyre char.
[145]	-	Wood, weed, plastic, carton, waste tyre-zeolite catalyst A4	2–3	1100	-	Oxygen	Analysis of the composition of the products obtained, during catalytic gasification of tyres and a mixture of various wastes.
[146]	Fixed bed	Waste tyre, pine bark	15 × 15	800–900	-	CO ₂	Evaluating the effect of gasification temperature and the blend ratio of two feedstocks on the yield of gas components.
[147]	Fixed bed	Scrap tyre, pine sawdust	20–30	–	-	Oxygen	Effect of co-gasification of different mixtures of tyre rubber and pine sawdust on the characteristics of the resulting gas products.
[148]	-	Tyre char	0.2–0.4	825–925	-	CO ₂	Evaluation of the kinetics of the gasification process of char from tyre pyrolysis using different kinetic models.
[149]	-	Tyre tread, sidewall tyre	~0.2	850–925	Atmospheric	CO ₂	Analyses of the effect of the presence of minerals contained in various tyre fragments on the gasification process.
[150]	-	Tyre char, rambutan peel	0.150–0.212	1127	-	CO ₂	Effect of different amounts of biomass additive on the kinetics of tyre char gasification process.
[151]	-	Plastic, paper, textiles, wood chips, RDF- tyre char	2–5	700–900	-	Air	The possibility of using tyre char as a potential catalyst for removing tar produced during the gasification of various materials and their mixtures.
[152]	TGA	Tyre char and ashes from corn cobs, beet pulp, sunflower husks, beech chips and coal	≤0.2	1100	0.1	CO ₂	Analysis of the effect of the presence of different amounts of fly ash and biomass ashes as potential sources of compounds showing catalytic activity in the gasification process, on the reactivity of tyre char.

Table 6. Cont.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[153]	Downdraft gasifier	Wood char, sewage sludge char, tyre char	–	1400	-	Air	Comparison of the gasification capabilities of three chars obtained from different raw materials.
[154]	Fixed bed	Tyre char	≤0.15	750–1050	Atmospheric	Steam	The effect of the concentration of the gasification agent, as well as the reaction time, on the gasification/activation process, including the conversion rates achieved and the kinetic parameters determined using various models.
[155]	-	Waste tyre	≤0.149	900–1100	-	CO ₂	Effect of temperature and particle size on the yield of the gas fraction obtained during gasification of used tyres.
[156]	Fixed bed	Tyre char	≤0.15	750–1050	-	CO ₂ , steam	Evaluation of the effects of temperature, activation duration and activation agent concentration on the structural properties of the tyre char.
[157]	-	Tyre char	≤0.2	1100	0.1	CO ₂	Influence of the type of atmosphere used during pyrolysis of waste tyres on the gasification process of the resulting tyre char.
[158]	-	MSW- Ni-tyre char, Fe-tyre char, Ni-Fe-tyre char	1–2	700–850	Atmospheric	Water form MSW	Evaluation of the feasibility of using nickel-iron catalysts applied to char from tyre pyrolysis by impregnation, during municipal waste gasification.
[66]	Fluidized bed	Waste tyre	–	700–850	-	Air, air + steam	Analysis of the effect of the type of atmosphere, the process temperature, and the ER equivalence ratio on the production of gaseous components during the gasification of used tyres.
[159]	Fixed bed	Tyre char, sunflower husk ash	<0.2	800–1000	0.5–1.0	Steam	Evaluation of the effect of conditions (pressure and temperature) on the process and kinetic parameters during steam gasification of tyre char in the presence of 5–15% sunflower husk ash as a catalyst.
[160]	Fixed bed	Tyre char, ashes from corn cobs, beet pulp, sunflower husks, beech chips	<0.2	800–1000	1.0	Steam	Evaluation of the effect of different biomass ashes addition as catalyst on the process and kinetic parameters during steam gasification of tyre char.
[161]	-	Pyrolysis oil from tyre	–	1000–1500	0.1–5.0	Oxygen/steam	Mass and energy balances for thermodynamic approach during the gasification of pyrolysis oil from tyre.

Table 6. Cont.

Reference	Reactor	Material /Catalyst	Particle Size [mm]	Temperature [°C]	Pressure [MPa]	Gasifying Agent	Description
[162]	-	Tyre oil	-	-		Nitrogen + oxygen	The addition of excess oxygen (25 vol) to the mixture lowers the solid fraction yield by converting some of the feedstock into gas.
[163]	Tubular reactor	Pyrolysis oil from a scrap tyre, dolomite, regenerated dolomite, Al ₂ O ₃ ^α	-	600–800		Steam	Evaluation of the feasibility of steam gasification of pyrolysis oil from a scrap tyres in the presence of a dolomite catalyst.
[164]	Plasma reactor	Pyrolytic oil from used tyres	0.5	1700		Steam/CO ₂ /O ₂	Effect of steam/plasma gasification of pyrolysis oil from tyre on gas composition.

In turn, Table 7 compiles the shares of solid, liquid, and gaseous products obtained during the study, as well as the composition of the latter depending on the process and raw material conditions. Upon scrutinizing Table 7, it becomes evident that the data pertaining to the proportions of solid, liquid, and gaseous fractions, as presented by the referenced authors, exhibit significant disparities. Determining the impact of variables on experimental outcomes based on this information is challenging, given the diverse timings, sample compositions, and experimental conditions under which the studies were conducted. Nevertheless, a discernible overall trend emerges. Specifically, in the gasification of pure rubber waste without additives, the solid fraction yield ranges from 8.9% in cases of catalytic gasification in an oxygen atmosphere [145] to 53.5% in instances of air gasification [74], averaging at 41.3%. The liquid fraction's share, averaging at 21.4%, varies from 5.3% in high-temperature steam gasification scenarios [131] to 41.5% [132] in experiments involving catalytic steam gasification. Concurrently, the gaseous fraction, averaging at 37.8%, exhibits variations from 14.3% in steam gasification at 600 °C [135] to 85.9% in steam gasification at 1000 °C [131]. Notably, when gasifying mixtures of rubber waste, other waste types, and biomass, a substantial variability in solid, liquid, and gaseous fraction yields is observed, attributable to the co-pyrolysis process [151].

Table 7. Shares of solid, liquid, and gas products, along with gas composition.

Reference	Gasifying Agent	Variable	Fraction [wt.%]				Gas Composition [vol.%]				
			Solid	Liquid	Gas	H ₂	CO	CO ₂	CH ₄	C ₂₊	
[131]	Steam	Temperature [°C]	850	43.4	27.0	34.7	51.5 *	6.1 *	3.0 *	30.3 *	9.1 *
			925	38.5	21.8	64.5	55.7 *	19.1 *	4.3 *	15.7 *	5.2 *
			1000	33.3	5.3	85.9	65.1 *	17.4 *	7.6 *	8.7 *	1.2 *
[132]	Steam	Catalyst addition	-	32.0	41.5	25.9	24.7	3.2	3.8	37.3	31.1
			Ni-Mg-Al	41.6	17.1	36.2	66.7	16.0	5.3	8.7	3.3
[137]	Steam	Ni/Al ₂ O ₃ catalyst addition	1 cycle				51.5 *	9.8 *	9.6 *	16.6 *	12.5 *
			2 cycles	41.7	31.9	39.8	41.5 *	9.2 *	10.9 *	22.1 *	16.3 *
			3 cycles				39.1 *	9.2 *	10.2 *	23.8 *	17.7 *
		4 cycles				39.9 *	9.5 *	11.5 *	21.4 *	17.7 *	
		Ni/dolomite catalyst addition	1 cycle				60.8 *	9.8 *	15.1 *	8.4 *	5.9 *
			2 cycles	38.0	32.7	50.1	52.7 *	8.2 *	13.3 *	15.0 *	10.8 *
			3 cycles				52.9 *	8.5 *	13.2 *	15.1 *	10.3 *
4 cycles					53.9 *	9.2 *	13.5 *	14.5 *	8.9 *		
[127]	Steam	Steam-tyres ratio [kg _{steam} /kg _{tyre}]	0.33	-	-	-	52.4	13.5	4.2	29.9	-
			0.50	-	-	-	55.8	16.0	5.9	22.3	-
			0.67	-	-	-	54.1	15.1	7.3	23.5	-
			1.00	-	-	-	56.3	14.9	8.5	20.3	-
			1.30	-	-	-	57.0	17.7	12.6	12.7	-

Table 7. Cont.

Reference	Gasifying Agent	Variable	Fraction [wt.%]			Gas Composition [vol.%]						
			Solid	Liquid	Gas	H ₂	CO	CO ₂	CH ₄	C ₂₊		
[133]	Steam	CeO catalyst addition at 500 °C	0	36.6	28.0	35.0	51.4 *	10.0 *	9.6 *	16.6 *	12.4 *	
			5	32.8	28.2	34.3	49.6 *	9.2 *	11.1 *	17.2 *	12.9 *	
			15	34.6	25.9	37.8	52.8 *	10.4 *	11.2 *	14.5 *	11.1 *	
			30	35.3	27.6	34.9	57.2 *	9.2 *	10.6 *	14.2 *	8.8 *	
			0	22.4	22.4	32.5	-	-	-	-	-	
			5	22.5	22.5	34.1	-	-	-	-	-	
		CeO catalyst addition at 750 °C	15	18.5	18.5	37.9	-	-	-	-	-	
			30	19.9	19.9	35.7	-	-	-	-	-	
			5	35.0	28.4	33.4	49.4 *	8.4 *	11.3 *	16.4 *	14.5 *	
		Ni catalyst addition at 500 °C	10	34.6	25.9	37.8	53.0 *	10.1 *	11.1 *	14.6 *	11.2 *	
			20	36.1	23.4	38.1	55.8 *	11.1 *	9.6 *	14.2 *	9.3 *	
			5	34.7	24.2	35.4	-	-	-	-	-	
		Ni catalyst addition at 750 °C	10	34.4	18.5	37.9	-	-	-	-	-	
			20	35.7	17.7	37.8	-	-	-	-	-	
0.5	41.7		31.9	39.8	51.5 *	9.8 *	10.5 *	17.0 *	11.2 *			
[135]	Steam	Catalyst: tyre ration [g/g]	1.0	45.3	16.9	44.4	62.5 *	12.1 *	7.2 *	12.1 *	6.1 *	
			1.5	50.3	15.2	58.2	63.4 *	17.6 *	7.7 *	8.5 *	2.8 *	
			2.0	52.3	8.7	51.2	68.2 *	17.6 *	7.9 *	5.6 *	0.7 *	
			600	43.3	38.6	14.3	62.1 *	5.2 *	7.3 *	8.6 *	16.8 *	
		Temperature [°C]	700	44.5	33.1	30.6	53.0 *	8.8 *	11.8 *	13.3 *	13.1 *	
			800	41.7	31.9	39.8	51.5 *	9.7 *	9.7 *	16.7 *	12.5 *	
			900	39.6	19.5	56.8	56.7 *	15.2 *	8.4 *	15.0 *	4.7 *	
			2.85	43.5	31.8	30.4	50.6 *	9.6 *	6.6 *	20.4 *	12.8 *	
		Water injected rate [g/h]	4.74	41.7	31.9	39.8	51.4 *	9.8 *	9.7 *	16.6 *	12.5 *	
			10.4	37.5	29.2	48.4	52.1 *	11.6 *	11.4 *	13.0 *	11.9 *	
			15.2	35.1	30.0	47.1	50.0 *	11.0 *	11.8 *	13.1 *	14.1 *	
			0.0	2.7	13.1	84.3	-	-	-	-	-	
		[151]	Steam	Wood chips/tyre char ratio	0.2	3.1	6.2	90.7	-	-	-	-
					0.5	1.2	7.7	91.1	-	-	-	-
1.0	2.4				4.7	93.0	-	-	-	-		
0.0	17.9				4.8	77.3	-	-	-	-		
Paper/tyre char ratio	0.2			15.7	7.1	77.2	-	-	-	-		
	0.5			15.4	4.5	80.2	-	-	-	-		
	1.0			16.2	5.0	78.8	-	-	-	-		
	0.0			2.7	4.6	92.7	-	-	-	-		
Textile/tyre char ratio	0.2			2.3	5.9	91.7	-	-	-	-		
	0.5			2.6	3.7	93.7	-	-	-	-		
	1.0			2.6	3.7	93.7	-	-	-	-		
	0.0			6.9	18.8	74.3	-	-	-	-		
Plastics/tyretyre char ratio	0.2			6.0	10.0	84.0	-	-	-	-		
	0.5			5.6	11.0	83.5	-	-	-	-		
	1.0			5.9	11.2	83.0	-	-	-	-		
	0.0			26.3	6.7	67.0	-	-	-	-		
RDF/tyre char ratio	0.2			25.8	7.4	66.8	-	-	-	-		
	0.5			25.8	7.3	67.0	-	-	-	-		
	1.0			25.8	8.0	66.2	-	-	-	-		
	0.0			2.7	13.1	84.3	-	-	-	-		
[129]	Steam	-	-	-	48.8	3.9	3.3	26.4	-			
	Air-steam	-	-	-	22.6	4.9	9.6	11.9	-			
	Air-CO ₂	-	-	-	30.7	5.5	12.8	15.6	-			
[145]	Oxygen	Zeolite A4 catalyst	8.9	24.7	64.3	9.8	0.1	0.3	8.0	53.8		
[158]	Water from MSW	Catalyst-Tyre Char	-	14.2 *	9.1 *	70.5 *	29.3 *	23.4 *	26.5 *	13.9 *	6.9 *	
			Ni	12.4 *	2.2 *	94.2 *	40.0 *	24.5 *	23.0 *	7.8 *	4.7 *	
			Fe	12.9 *	2.8 *	91.8 *	38.2 *	22.0 *	25.5 *	9.4 *	4.9 *	
			Ni-Fe	12.6 *	2.5 *	96.6 *	42.2 *	21.1 *	23.5 *	9.0 *	4.2 *	
[74]	Air	Air flow rate 0.05 L/min	600 °C	51.2	11.1	37.7	-	-	-	-		
			700 °C	49.2	11.8	39.2	-	-	-	-		
			800 °C	51.1	12.4	36.5	-	-	-	-		
			600 °C	50.6	15.8	33.6	-	-	-	-		
		Air flow rate 0.10 L/min	700 °C	48.0	15.8	36.2	-	-	-	-		
			800 °C	53.5	13.5	33.0	-	-	-	-		
			600 °C	48.8	19.1	32.1	-	-	-	-		
			700 °C	50.6	17.1	32.3	-	-	-	-		
		Air flow rate 0.20 L/min	800 °C	49.7	10.7	39.6	-	-	-	-		
			600 °C	47.4	15.8	36.8	-	-	-	-		
			700 °C	46.1	19.2	34.7	-	-	-	-		
			800 °C	43.1	15.8	41.1	-	-	-	-		
		Air flow rate 0.30 L/min	600 °C	50.9	14.5	34.6	-	-	-	-		
			700 °C	47.3	19.0	33.7	-	-	-	-		
			800 °C	48.8	16.0	35.2	-	-	-	-		
			600 °C	50.1	18.3	31.6	-	-	-	-		
		Air flow rate 0.40 L/min	700 °C	47.2	20.8	32.0	-	-	-	-		
			800 °C	47.8	17.8	34.4	-	-	-	-		
			600 °C	53.0	8.2	38.8	-	-	-	-		
			700 °C	50.4	12.7	36.9	-	-	-	-		
Oxygen	Oxygen flow rate 0.01 L/min	800 °C	52.1	10.7	37.2	-	-	-	-			

Table 7. Cont.

Reference	Gasifying Agent	Variable	Fraction [wt.%]			Gas Composition [vol.%]					
			Solid	Liquid	Gas	H ₂	CO	CO ₂	CH ₄	C ₂₊	
[122]	Air	Equivalence ratio 0.2	560 °C	-	-	-	16.9 *	41.7 *	14.8 *	9.8 *	16.8 *
			650 °C	-	-	-	17.4 *	25.4 *	15.5 *	13.0 *	28.7 *
			720 °C	-	-	-	11.9 *	18.0 *	15.9 *	15.1 *	39.1 *
		Equivalence ratio 0.4	800 °C	-	-	-	11.4 *	18.2 *	17.0 *	14.9 *	38.5 *
			470 °C	-	-	-	4.8 *	53.6 *	31.4 *	2.4 *	7.8 *
			550 °C	-	-	-	13.8 *	32.7 *	30.5 *	7.9 *	15.1 *
		Equivalence ratio 0.6	630 °C	-	-	-	17.0 *	22.3 *	30.0 *	4.9 *	25.8 *
			710 °C	-	-	-	10.8 *	16.1 *	27.3 *	11.8 *	34.0 *
			430 °C	-	-	-	1.6 *	36.5 *	54.1 *	2.3 *	5.5 *
			550 °C	-	-	-	7.2 *	29.1 *	47.8 *	6.9 *	9.0 *
			600 °C	-	-	-	7.4 *	22.4 *	41.9 *	5.1 *	23.2 *
			700 °C	-	-	-	4.4 *	17.3 *	38.5 *	10.1 *	29.7 *
[163]	Steam	Non-catalytic	800 °C	-	-	-	24.7	4.4	3.1	24.0	-
			600 °C	-	-	-	44.0	0.2	0.0	8.8	-
		Dolomite	700 °C	-	-	-	56.5	0.8	0.0	9.7	-
			800 °C	-	-	-	60.6	5.2	9.2	13.0	-
		Regenerated dolomite	800 °C	-	-	-	61.5	5.6	9.2	11.7	-
			800 °C	-	-	-	54.5	5.7	9.8	11.9	-
[164]	Plasma/Steam	-	-	-	-	58.0	32.0	4.0	5.0	-	
	Plasma/CO ₂	-	-	-	-	27.0	53.0	16.0	3.0	-	
	Plasma/O ₂	1700 °C	-	-	-	48.0	47.0	3.0	1.5	-	
	Plasma/CO ₂ + O ₂	-	-	-	-	19.0	54.0	25.0	1.5	-	

* Data read from graphs.

5.1. The Course of the Used Tyre Gasification Process

During the gasification process of used tyres, two basic stages can be distinguished related to mass loss during the thermogravimetric test shown in Figure 5:

- Stage I, which occurs in the temperature range of about 250 to 550 °C, the accompanying mass loss is about 60%. This loss is associated with pyrolysis, resulting from the degradation of natural and synthetic rubber, with the total content in tyres ranging from 40 to 50%, along with the release of volatile compounds, i.e., carbon monoxide and carbon dioxide, methane, hydrogen, and sulphur oxide IV [30,128].
- Stage II is associated with the gasification reactions between the high elemental carbon tyre char formed in the first stage and the gasification agent. This stage begins at a temperature of about 800–850 °C and continues until the elemental carbon is fully reacted. During this stage, a significant intensification of the formation of gaseous components is observed, the composition of which depends primarily on the gasification agent used [30,128].

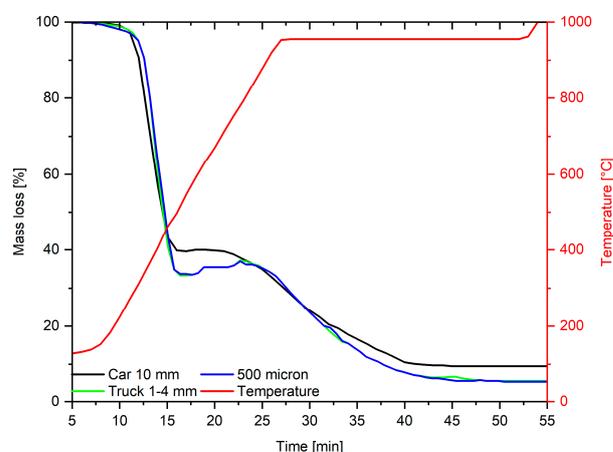


Figure 5. Thermogravimetric analysis of waste tyre gasification (based on [30]).

In the case of direct gasification of tyre char, the first stage is not observed, or its contribution is marginal, and the main role is played by the gasification reactions of

the tyre char with the gasification agent. Betancur et al. [148] demonstrated two sub-stages associated with changes in the reaction rate (dX/dt) as a function of conversion (X) (Figure 6). The first sub-stage, observed as a drastic decrease in the reaction rate to about 20% conversion, according to the authors, is related to the release of volatile substances and inorganic compounds contained in the char, which is significantly influenced by morphological properties, as well as by the presence of potential catalytically active elements contained in the ash. During the second sub-stage, there is stabilisation and a slow decrease in the reaction rate until the tyre char is completely over-reacted, with dX/dt reaction rate values significantly lower compared to the first stage. In addition, it has been shown that as the temperature increases, the reaction rate increases, especially during the first sub-step.

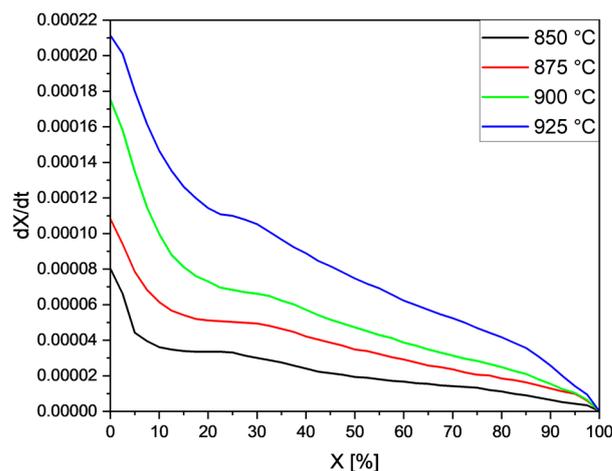


Figure 6. Changes in the reaction rate during the gasification of tyre char (based on [148]).

5.2. Effects of Temperature

Temperature is by far the most important parameter determining the gasification of waste tyres, as it has the greatest impact on the rate of the process, as well as the yields of the various products. Based on the data presented in Table 7, it can be concluded that, in general, as the process temperature increases, there is an increase in the proportion of gaseous products and a decrease in the liquid fraction. Portofino et al. [131] showed that increasing the temperature during steam gasification of rubber from used tyres from 850 °C to 1000 °C results in an increase in the share of the gas fraction from 34.7 wt.% to 85.9 wt.%. At the same time, there is a sharp decline in the share of liquid products from 27.0 wt.% to 5.3 wt.%, as well as solids from a value of 43.4 wt.% to 33.3 wt.%. An increase in the share of gaseous products at the expense of a decrease in the share of the liquid fraction as the temperature increased from 600 °C to 900 °C was also observed by Elbaba and Williams [135], with no such significant decrease in the proportion of solid products. A different situation was observed in the study by Ongen et al. [74] because the shares of the liquid fraction generally increase with increasing temperature, while the shares of gaseous and solid products fluctuate only slightly. The authors attribute the increase in the amount of liquid phase formed to the use of a fixed-bed reactor, which can result in hindered contact between the gasification agent and the material, as well as inhomogeneous temperatures across the bed. In general, it can be concluded that an increase in the gasification temperature leads to an increase in the degree of conversion, resulting in an increase in the yield of gaseous products such as CO, CO₂ or H₂; however, as shown by the results presented by Ongen et al. [74], there may be deviations as a result of some technological solutions that favour the production of the liquid fraction. In the case of light hydrocarbons, decomposition occurs with the release of simpler inorganic components and hydrogen. Nanda et al. [142] showed an increase in yields of each of the gas components under subcritical and supercritical conditions during steam gasification, with hydrogen, carbon dioxide, and methane being the main contributors. Portofino et al. [134] obtained an

increase in hydrogen, carbon monoxide and carbon dioxide concentrations while decreasing light C_1 – C_2 hydrocarbons during the steam gasification of used tyres. On the other hand, Song et al. [155] and Wang et al. [146], studying the gasification process of used tyres in an atmosphere of carbon dioxide, obtained higher shares of CO and H_2 , while observing lower shares of CO_2 and light C_{2+} hydrocarbons. The significant effect of the temperature of gasification of used tyres on the shares of various fractions and the composition of the obtained syngas leads to changes in the values of parameters describing the efficiency of the process, as well as the quality of the obtained gas. Nanda et al. [142] show that increasing temperature leads to an improvement in catalytic gasification efficiency from 9.5% at 325 °C to 32.8% at 625 °C. Policella et al. [143] also showed an improvement in cold gas efficiency with increasing gasification temperature. In addition, Policella et al. [143], as well as Portofino et al. [131], observed that as the temperature increases, there is a decrease in the higher heating value of the resulting syngas with respect to its volume, while this parameter improves with respect to mass, which is due to an increase in the yield of the gaseous components.

In the case of the gasification of char from tyre pyrolysis, the process is ultimately carried out until the elemental carbon is completely reacted. Only gaseous products and solid residue (ash or slag with any unreacted organic part of the tyre char) are obtained. Authors of papers on the gasification of tyre char note its low reactivity compared to other raw materials, which is associated with low conversion [118,119,138,140,144,153,154] (example curves of the degree of conversion as a function of time are shown in Figure 7). The increase in temperature during the gasification of tyre char primarily leads to an improvement in the degree of conversion and reduces the time required to achieve complete conversion. Preciado-Hernandes et al. [144] subjected tyre char to gasification/activation in the temperature range from 750 °C to 950 °C with carbon dioxide as the gasification agent. Despite the significant reaction time of 6 h, the carbon conversion degree did not exceed 20% at 750 and 850 °C. Using a temperature of 950 °C allowed the conversion rate to increase, but it did not exceed 60%. Preciado-Hernandes et al. [154] also performed similar gasification measurements using steam as the gasification agent. Similar values for the degree of carbon conversion were obtained but with a reaction time of 4 h, indicating the higher reactivity of the tested tyre char towards this gasification agent. The authors of both papers also compared the obtained values of the reactivity index $R_{0.5}$ with literature values for low-reactivity carbon raw materials such as anthracite or bituminous coals. The tyre chars had the lowest indexes, indicating that they are a low-reactivity materials. Similarly, low values for the maximum conversion degree were also obtained by Lahijani et al. [136] because the determined values at 850 and 900 °C did not exceed 20 and 50%, respectively. A further increase in temperature to 950 °C allowed higher conversion degrees exceeding 90% to be achieved, with a marked reduction in reaction time achieved only at 1000 °C. Gurai [138] and also Issac et al. [140] performed gasification measurements of tyre char and chars obtained from coals in the atmosphere of CO_2 to compare the reactivity of these materials. The conversion degree curves obtained showed that each of the raw materials used completely reacted at the set temperatures; however, in the case of the gasification of the tyre char, the curves shifted towards longer reaction times throughout the process. Activation energy values reported in the literature, obtained using various kinetic models, showed that tyre char has the highest values of this parameter among the other materials analysed, which also confirms its low reactivity [136,141,144,150,154]. The low reactivity of the tyre char may be due to its high elemental carbon content, low value of structural parameters and low content of catalytically active compounds [140,148,165,166]. Due to the low reactivity of tyre char, it may require the use of catalysts during the gasification process, especially at lower temperatures [152,159].

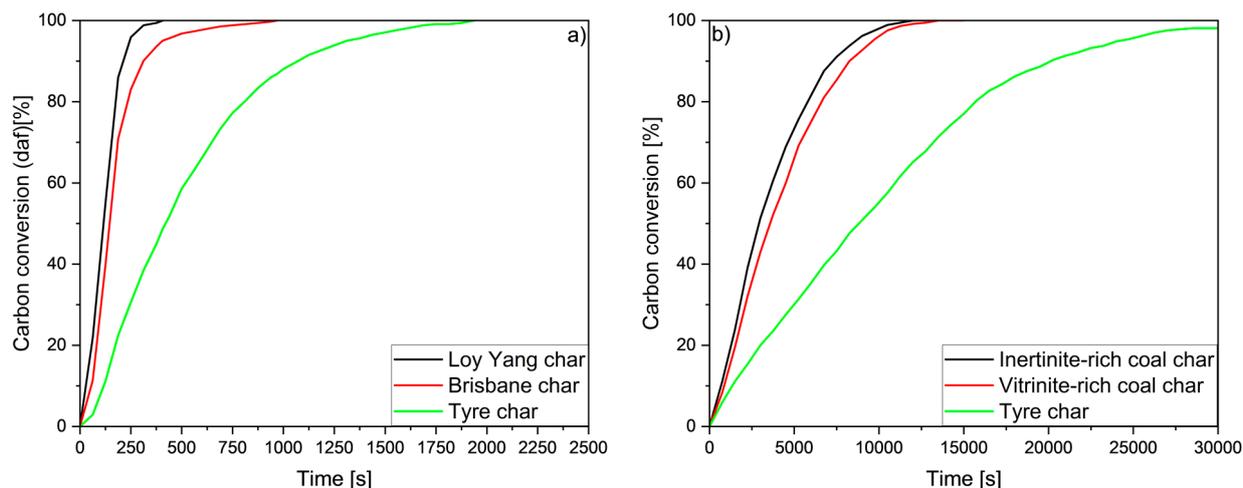


Figure 7. Comparison of carbon conversion curves for char from used tyre and coal, based on (a) [140], as well as (b) [138].

5.3. Effects of Heating Rate

The heating rate is also an important factor affecting the course and duration of the gasification process. It can be seen that a higher heating rate results in a shift of thermogravimetric curves toward higher temperatures. This is due to the limitation of heat transfer, and these differences are greater the higher the heating rates are, resulting in the reaction onsets observed in thermogravimetric curves being in the higher temperature region [167]. When gasifying tyre char in the atmosphere of CO_2 , Czerski et al. [152] obtained the maximum conversion rate at about 1040°C for a heating rate of $3^\circ\text{C}/\text{min}$, while increasing the heating rate to 10 and $15^\circ\text{C}/\text{min}$ resulted in the maximum conversion being achieved at temperatures exceeding 1090°C . Similar results in their paper were obtained by Lahijani et al. [141], who subjected tyre char to gasification in the atmosphere of carbon dioxide, showing that as the heating rate increases, the difference between the temperatures determining the beginning and end of the gasification reaction increases. In addition, the DTG curves compiled by Song et al. [155] show that as the heating rate increases, the mass loss rate increases, which implies that the gasification reaction rate increases too. This is also confirmed by the tabulated values of the maximum mass loss rate, which increase together with the increasing heating rate from 17.5 to $35.0\%/ \text{min}$.

5.4. Effects of Total Pressure

So far, only a few papers have been published on the effect of total pressure on the rubber waste gasification process. In their study, López et al. [130] subjected tyre char derived from the distillation of tyre pellets to steam gasification at total pressures of 0.1 and 1.5 MPa at 1000°C . The effect of pressure on the composition and characteristics of the obtained gas fraction was analysed, and the results were related to coals with different degrees of metamorphism. The obtained gas product concentration results showed that carbon monoxide is the main component of the gas, regardless of the set pressure. The increase in pressure promoted an increase in the yield of all gaseous products, with CO and H_2 being the most affected, increasing from 16.9 to 18.0 and from 11.7 to 12.7 vol.%, respectively. However, such a small increase in yields of CO and H_2 may be due to the range of reproducibility during experiments. The increase in the yield of the combustible components of the gas results in an increase in the higher heating value of the gas obtained by $0.4 \text{ MJ}/\text{Nm}^3$, while it is worth noting that, regardless of the pressure, the higher heating values obtained for the tyre char are the lowest of all the materials tested. However, tyre pyrolysis char is the only material that was accompanied by an improvement in the conversion degree from 87.5 to 97.5% as the gasification pressure increased. Śpiwak et al. subjected tyre char to steam gasification in the presence of sunflower husk ash as a catalytic

additive in amounts of 5, 10, and 15 wt.% at temperatures of 800, 850, 900, and 1000 °C, and at pressures of 0.5, and 1.0 MPa [159]. The authors noted an increase in the formation rate and yield of CO with increasing pressure, which has been linked to an increase in the number of active sites on the surface of the tyre char, as well as the promotion of heterogeneous gas-solid reactions. In the case of hydrogen, the effect of pressure was ambiguous, as there are also homogeneous reactions in the gas phase. The H₂ yield in the 800–850 °C temperature range was higher at higher pressures, while no such effect was observed at higher temperatures. The evaluation of the effect of pressure on the course of the conversion degree curves carried out showed an increase in the reaction rate for tyre char gasified at higher pressure, especially in the low temperature range, which is also confirmed by the compiled higher reactivity index value $R_{0.5}$ at a pressure of 1.0 MPa. In addition, higher activation energies were recorded at higher pressures, accompanied by a parallel increase in the value of the pre-exponential factor. The increase in the latter compensates for higher values of activation energy, ultimately having a positive effect on the pressure-induced reactivity of tyre char during steam gasification.

5.5. Effects of the Amount of Gasification Agent

Another factor that exerts an influence on the course of the gasification reactions and the composition of the resulting products is the amount of gasification agent fed. Both used tyres [127,135] and the derived tyre char [144,148,154] were tested for this, and the results are compiled in Table 7. Donatelli et al. [127] analysed the effect of the steam-to-feedstock ratio (FR) in used tyres on the composition of the resulting gas. They noted a significant increase in hydrogen, carbon monoxide, and carbon dioxide content, as well as a decrease in the methane volume with increasing FR values, which is due to the steam reforming reaction of methane. Elbaba and Williams [135] studied the effect of the steam flow rate on the yield of individual products and the composition of the resulting gas and showed that as the amount of steam fed increased, the share of gaseous products increased, while the amount of liquid products formed and the solid fraction decreased. Analysing the composition of the gas, a slight increase in the concentration of hydrogen, carbon monoxide and carbon dioxide can be observed, while the optimum content of gaseous components was obtained at a steam flow rate of 10.4 g/h, which is due to the reforming reaction of methane and light C₂–C₄ hydrocarbons. At a steam feeding of 15.2 g/h, a decrease in hydrogen and carbon monoxide concentrations is observed at the expense of an increase in CO₂ and CH₄, which the authors believe is responsible for the reversed water gas reaction, as well as the methanation reaction. Preciado-Hernandez et al. [144,154], in their papers on the gasification/activation of tyre char in the temperature range of 750–1050 °C and in atmospheres of CO₂, as well as H₂O at concentrations of these gases at 33.3, 50.0, and 66.7 vol.%, showed that an increase in the concentration of the gasification agent positively affects the conversion degree at specific time intervals. This effect is more pronounced as the process temperature increases. This is confirmed by the values of the reactivity index $R_{0.5}$ compiled on the charts, as higher values of this parameter were obtained, indicating greater reactivity with increasing concentrations of CO₂ and H₂O. This effect is more evident as the gasification temperature increases. For the same temperature conditions, higher $R_{0.5}$ values were obtained using steam, confirming the higher reactivity of tyre char to H₂O compared to CO₂. Analogous results were also obtained by Betancur et al. [148] during the gasification of tyre char in the presence of carbon dioxide, analysing the effect of CO₂ concentration on the conversion degree curves and reaction rate at 900 °C. An increase in the content of the gasification agent makes the curves steeper, and the maximum conversion degree is reached more quickly, confirming the higher reactivity of the raw material. This effect is also evident in the graph of changes in the reaction rate as a function of the conversion degree, suggesting that a higher reaction rate is achieved, especially in the first half of the carbon-steam reaction.

5.6. Effect of Particle Size

Literature reports on the effect of the particle size of rubber waste materials indicate that as the size decreases, there is an increase in the specific surface area, as well as the pore volume, which is an important parameter that has an impact on the diffusion rate, the conversion degree, and consequently on reactivity [168]. Kandasamy and Gökalp [30] performed measurements including thermogravimetric gasification of used tyres from a truck with particle sizes of <0.5 and 1–4 mm, respectively. The TG curves obtained do not show significant differences in the course of mass loss by overlapping, and the slight deviations during the gasification of the produced tyre char may be due to the aforementioned morphological changes, as well as the limitation of heat and mass transfer [168,169]. Leung and Wang [116] analysed the effect of particle size on product yields when gasifying a used tyre in the atmosphere of air in a fluidised bed reactor. The results show that as the particle size decreases, the yield of liquid and gaseous products increases at the expense of a decrease in the yield of the solid fraction. Analysing the concentrations of individual gas components, one can note an increase in the concentration of carbon monoxide and methane in particular, while no significant changes are observed for hydrogen and C_xH_y gas hydrocarbons. Consequently, an increase in the degree of fragmentation of the used tyre results in an increase in the calorific value of the resulting gas. Based on the results obtained, the authors also indicate that the optimal particle size for fluidised bed gasification varies between 1.5–2.0 mm. Song et al. [155], investigating the effect of tyre rubber particle size on the yield of gaseous components during gasification in the atmosphere of CO_2 , showed an increase in the yields of carbon monoxide, in particular from 14.1 vol.% to 18.7 vol.%, as well as hydrogen, from 12.4 to 15.8 vol.% with an increasing degree of fragmentation. In addition, there was a slight increase in the methane yield, while the amount of carbon dioxide formed decreased. The increase in yields of the combustible components of the gas translates into an improvement in its calorific value. In turn, Karatas et al. [129], while gasifying used tyres in a mixed atmosphere of CO_2 and air in a fluidised-bed reactor, also obtained higher concentrations of hydrogen and carbon monoxide for smaller particle sizes. This favourably affected the calorific value of the syngas. According to the authors, this is due to impeded heat transfer between the gas phase and tyre particles at larger particle size, resulting in incomplete devolatilisation.

5.7. Effect of Surface Morphology and Mineral Matter

There are also several papers in the literature on the influence of the textural properties of tyre char on the gasification reaction. Issac et al. [140] compared the parameters determining the course of the gasification reaction obtained for raw tyre char and acid-washed tyre char (without mineral content), as well as for chars produced from two lignites. The morphological analysis of the obtained chars showed that the raw tyre char had the lowest internal surface area value of $31.3 \text{ m}^2/\text{g}$, and it was $4.5 \text{ m}^2/\text{g}$ lower than that of the acid-washed tyre char and about 10 times lower compared to the lignite chars. On the other hand, the results regarding the size of the average pore radius showed that it was $3.21 \times 10^{-5} \text{ m}$ for the raw tyre char. This is one order of magnitude smaller than for the mineral-free tyre char and three orders of magnitude smaller compared to the values obtained for the lignite chars. From the course of the conversion degree curves, it can be concluded that tyre char is the least reactive raw material subjected to gasification, regardless of the set temperature value. In addition, despite the greater internal surface area that characterises acid-washed tyre char, it is much less reactive compared to raw tyre char, especially for temperatures in the 1000–1200 °C range. This is also confirmed by the calculated values of activation energy, where the highest values were obtained for the mineral-free tyre char, confirming its low reactivity. This suggests that the specific surface area of the tyre char is not a key criterion determining reactivity. The authors indicate that catalytically active elements contained in the mineral matter play an important role in gasification reactions. Preciado-Hernandes et al. [144,154], in their analysis of the gasification/activation of tyre char in the atmospheres of CO_2 and H_2O , evaluated the degree of fit of various kinetic

models to experimental data, showing the change in the conversion degree as a function of time for different concentrations of gasification agents at 1000 °C. Among the models used, the volumetric model had the highest degree of fit, indicating that the heterogeneous reaction between the gasification agent and elemental carbon is independent of the pore structure.

5.8. Char Activation

The production of activated carbon from waste tyres char by physical activation is usually carried out using steam or carbon dioxide [117,120,123,125,156,170]; however, it is possible to use oxygen or nitric oxide II [125]. Activation is a process that leads to improved textural properties. As mentioned above (Table 5), tyre chars from pyrolysis have relatively low structural property parameters, which could potentially affect their limited reactivity during gasification. It may also limit their adsorption capacity for possible use as sorbents used to separate solid, liquid, and gaseous phases such as heavy metals, herbicides, pesticides, petroleum pollutants, or dyes from wastewater [120,170–172]. López et al. [125], in a study of the activation of tyre char in the atmosphere of steam, point to the high reactivity of the raw material, which has been attributed to the catalytic action of ash components like ZnO. In addition, a temperature increase from 850 to 900 °C results in an approximately twofold increase in the rate of activation. Gonzalez et al. [120] and Lopez et al. [125] also noted a linear relationship between the activation time and the conversion degree of the tyre char regardless of the set temperature. Similar results of the linear dependence of the degree of conversion on time were obtained by Betancur et al. [123], who subjected tyre char to activation, but in the presence of CO₂. The study also showed an increase in specific surface area and total pore volume with an increase in activating agent flow rate from values of 88.0 m²/g and 0.14 cm³/g obtained at 50 mL/min to 414.5 m²/g, and 0.33 cm³/g obtained at 150 mL/min, respectively. In turn, Zhang et al. [156] analysed the effects of atmosphere, the conversion degree, and temperature (950 and 1050 °C) on the development of the porous structure of chars from used tyres during its activation with steam and CO₂. As can be seen from the results compiled in Figure 8, higher values of morphological parameters (surface area—BET and pore volume) were obtained with the use of steam. This may be attributed to the easier diffusion of steam molecules, caused by their smaller size compared to CO₂ molecules [125]. In addition, an increase in temperature decreases the BET value, and the difference increases as the carbon conversion degree increases. In contrast, no significant effect of temperature is observed on the total volume of pores and mesopores. The volume of micropores, which make up only a small percentage of the structure, is larger for lower temperatures at low conversion degrees, though a significant increase in their volume is observed, after which it decreases significantly. The authors explain this by the widening of micropores, which caused the collapse of the walls between them due to the conversion of elemental carbon. The compiled graphs confirm that when the volume of micropores decreases, the volume of mesopores clearly increases. In addition, higher temperatures result in smaller micropore volumes due to the collapse. This also explains the higher BET values obtained at lower temperatures [156].

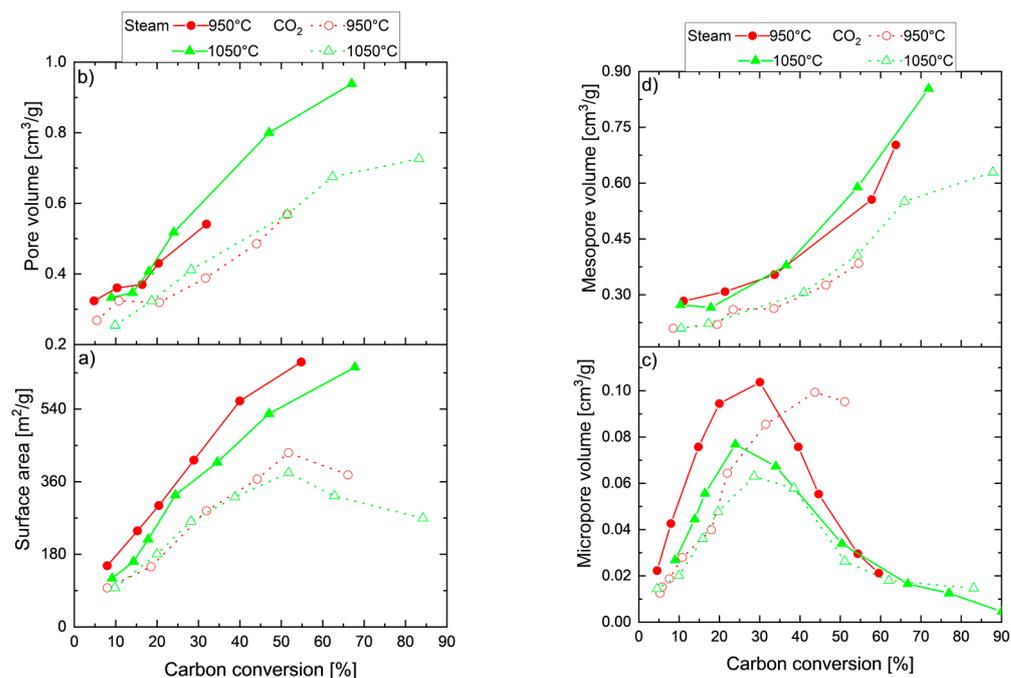


Figure 8. Development of morphology parameters during steam/CO₂ activation of tyre char: (a) surface area; (b) pore volume; (c) mesopore volume; (d) micropore volume (based on [156]).

5.9. Effect of Catalysts

To ensure the most efficient and complete conversion possible during gasification, especially for such unreactive materials as tyre chars, studies are being conducted into the feasibility of using catalysts through the direct addition of catalytically active compounds, as well as co-gasification. As shown in Table 7, during the gasification reaction of used tyres, the addition of the active substance allows the yield of gaseous products to increase, primarily lowering the yield of liquid products including tar. Elbaba and Williams [135] investigated the effect of the catalyst–tyre ratio on the yields of the various fractions and the composition of the major gas products, using a nickel catalyst deposited on an alumina support. The analysis of the products showed that an increase in the proportion of catalyst leads to a significant increase in the yield of gaseous products and the solid fraction, while reducing the yield of the liquid fraction. In addition, a continuous increase in the shares of hydrogen and carbon monoxide was observed with a near-linear decrease in the concentration of light hydrocarbons C_nH_m. Elbaba et al. [132] also tested the feasibility of using a Ni–Mg–Al catalyst for the gasification of used tyres in the atmosphere of steam. The results show that, compared to the process carried out without the addition of a catalyst, higher solid and gas fraction yields were obtained at the expense of a reduction in liquid product yields. The analysis of the composition of the gas obtained showed a nearly fivefold increase in CO concentration, from 3.2 vol.% for the process without the addition of a catalyst to 16.0 vol.% obtained in the presence of a catalyst. Additionally, there was a more than twofold increase in hydrogen concentration, from 24.7 vol.% to 66.7 vol.%, respectively. A nickel–magnesium catalyst on an aluminium support reduces the concentration of not only liquid hydrocarbons, but also gaseous C_nH_m from a value of 68.4 vol.% to 12.01 vol.%. Elbaba et al. [133] also performed gasification studies of used tyres in the presence of various amounts of cerium oxide (CeO₂) and nickel (Ni) on an aluminium support calcined at temperatures of 500 and 750 °C. The authors obtained an increase in the yield of gaseous components when the CeO₂ content increased from 5 to 15 wt.%, while further increases in the amount of catalyst resulted in a decrease in the yield of this fraction. A higher increase was recorded when the calcination temperature of the catalyst was 750 °C. In addition, the use of cerium oxide as a catalyst did not significantly effect changes in the concentrations of gaseous components except for a slight increase in hydrogen concentration. The yield

of gaseous components and hydrogen also increased with increasing Ni content, and a higher increase was obtained when the calcination temperature was 500 °C. However, the authors point out the deactivation of catalysts during tyre gasification, resulting primarily from the presence of sulphur compounds contained in the tyre in gasification reactions forming, among other products, H₂S, which adsorbs on the surface of metals to form a sulphur layer that inhibits the chemisorption of the gasification agent, thereby deactivating the catalyst [137]. The second cause of catalytic deactivation is the deposition of elemental carbon on the metal surface. A study of several applications of Ni/Al₂O₃ and Ni/dolomite catalysts during pyrolysis–gasification of a used tyre in a steam atmosphere showed less deactivation of the dolomite catalyst in successive cycles of operation [137]. The authors indicate that the use of a Ni/dolomite catalyst results in less carbon deposition on the metal, suggesting that the alkalinity of the dolomite reduces carbon deposition on the metal surface. Nanda et al. [142] used Mg(OH)₂, Ca(OH)₂, Ba(OH)₂, Ru/Al₂O₃, and Ni/SiO₂-Al₂O₃ catalysts during subcritical and supercritical tyre gasification. The presence of catalysts significantly contributed to improving the efficiency of the process, as well as the overall yield of gas products. Interestingly, the highest selectivity for hydrogen production was obtained with the addition of alkaline earth metal hydroxide catalysts, ranging from 83.4% for Mg(OH)₂ to 99.7% for the barium hydroxide catalyst. As the authors point out, this is due to the fact that hydroxide catalysts capture CO₂, resulting in a decrease in the concentration of this gas component. However, the presence of Ru/Al₂O₃ catalysts, as well as that of Ni/SiO₂-Al₂O₃ catalysts, resulted in the highest increase in yields of gaseous components, including hydrogen, methane, light hydrocarbons, and carbon dioxide. Czerski et al. [152] used biomass ashes (corn cobs, beet pulp, sunflower husks, beech chips) with a high content of alkali metals and alkaline earth metals as potential catalysts during the gasification of tyre char in the atmosphere of CO₂. The ashes used contributed to an increase in the reactivity indexes of char gasification, i.e., a reduction in the temperature required to achieve 50% conversion, as well as an increase in the values of reaction rate constants calculated at 900 °C. The effect of the amount of catalytic additive (5, 10, and 15% by weight) was also analysed, and the positive effect was more pronounced with higher biomass ash content, resulting in a shift of thermogravimetric curves toward lower temperatures. The greatest improvement in the CO₂ gasification rate of tyre char was achieved with sunflower husk ash, which has the highest K₂O content. Śpiewak et al. [159] also studied the effect of sunflower husk ash addition at 5, 10, and 15 wt.% on the course of steam gasification of tyre char using the thermovolumetric method in the temperature range of 800–1000 °C and at pressures of 0.5 and 1 MPa. Based on the analysis of the rate curves for the formation of CO and H₂, an increase in the intensity of their formation in the catalytic process was noted. The presence of the catalyst and an increase in the amount of catalyst also contributed to an improvement in the reaction rate, as confirmed by the conversion degree curves and the R_{0.5} reactivity index values, especially for temperatures of 800–900 °C, at both pressures. In addition, the significant content of active compounds present in sunflower husk ash (45.4% K₂O and 24.4% CaO) promoted hydrogen formation, especially at low temperatures of 800–850 °C. The catalyst used also had a positive effect on the obtained values of the kinetic parameters of the gasification reaction, i.e., the activation energy and pre-exponential factor. Continuing their studies, Śpiewak et al. [160] assessed the feasibility of steam gasification of tyre char and the impact of various biomass ashes (sunflower husk, beet pulp, beech chips and corn cobs in the amounts of 5, 10 and 15 wt.%) in the process. Tyre char and char-catalysts were subjected to gasification at temperatures ranging from 800 to 1000 °C and at a pressure of 1 MPa. Changes in the formation rates of the main gas components, maximum carbon conversion, half-times conversion, yields, composition of gas components, and H₂/CO ratio were determined. Kinetic parameters were calculated using the grain and random pore models. The addition of a catalyst and increasing its loading improved the reactivity of the tyre char at up to 850 °C and had a significant, but temperature-dependent, impact on gas component yields. Performing catalytic tyre char gasification under appropriately selected conditions (800–850 °C and

10/15 wt.% of sunflower husk and beech chips ash as catalysts) may be an attractive way to efficiently obtain a hydrogen-rich gas.

As mentioned above, there are reports in the literature of co-gasification of tyre waste-based material together with other raw materials, mainly various types of biomass [136,139,141,146,147,150], lignite char [126] or sewage sludge [20,121]. Al-Rahbi and Williams [139] pyrolysed and then gasified biomass in the presence of tyre char, in the atmosphere of steam. The results showed an increase in the production of the gas fraction, especially hydrogen and carbon monoxide, with the increase being more pronounced for the tyre char not washed with acid, confirming that the elements contained in the mineral matter of tyre char have a significant catalytic effect. In addition, the authors point out that the presence of char from tyre pyrolysis promotes tar steam reforming reactions. Yang et al. [147] analysed the effects of co-gasifying used tyres and pine sawdust in the presence of air. The results presented in their study show an increase in the yield of gaseous products, especially hydrogen, carbon monoxide and methane, with the increasing addition of used tyres. Consequently, there is also an increase in the calorific value of the resulting gas. In addition, the calculated values of kinetic parameters show that the presence of biomass results in a reduction in the activation energy from 40.9 kJ/mol for a sample of char alone to 24.9 kJ/mol at a ratio of used tyres to pine sawdust of 1:1. Wang et al. [146] on the other hand, investigated the possibility of co-gasifying used tyres and pine bark in various proportions in the atmosphere of carbon dioxide. The analysis of gas component yields showed that the addition of biomass increases the yields of hydrogen and carbon monoxide, and decreases the yield of light hydrocarbons C_mH_n , with the described changes being more pronounced at higher temperatures. The compiled CO_2 consumption values at 800 °C indicate similar reactivity regardless of the type of gasified mixture. However, increasing the temperature to 900 °C results in an increase in carbon dioxide consumption as the biomass content of the mixture increases, while confirming the low reactivity of the tyre char. Lahijani et al. [136] subjected tyre char (which also underwent an acid washing operation to remove mineral matter) to gasification along with admixtures of almond hull chars and the addition of palm empty fruit bunches in the atmosphere of CO_2 . The presence of 10, 30 and 50% biomass chars resulted in an increase in the reactivity of the char (improvement of the maximum conversion degree), as well as a reduction in the reaction time. Conversion curves obtained for mixtures (in a 1:1 ratio) of the biomass chars and mineral-free tyre char showed significantly lower reactivity, as shown by the lower slope of the conversion curves, compared to those obtained for samples not washed with acid. According to the authors, the increase in reactivity for mixtures of biomass and tyres including those not acid-washed is most likely due to the presence of alkali metal elements and alkaline earth metals such as Na, K, Mg, or Ca, showing catalytic activity. This is also confirmed by the compiled kinetic parameters obtained using the modified random pore model. The lowest activation energy values were obtained for mixtures of 50% almond shell and tyre char (203.3 kJ/mol) and 50% palm empty fruit bunches and tyre char (187.6 kJ/mol). Also, Lahijani et al. [150] showed that the addition of various amounts of rambutan peel (from 15 to 85%), which is rich in catalytically active components, during thermogravimetric gasification of tyre char in the presence of CO_2 , causes a gradual decrease in the activation energy from a value of about 280 kJ/mol to about 220 kJ/mol. Lahijani et al. [141] also performed thermogravimetric gasification of tyre char with the addition of biomass derived from cattle manure, palm empty fruit bunch handfolds, almond hulls, and rubber seed hulls. Regardless of the set heating rate, the compiled TG curves and the characteristic temperatures read from them, i.e., beginning of weight loss, maximum weight loss, and end of weight loss, were clearly shifted toward lower temperatures, showing an increase in the reactivity of the tyre char. In addition, lower activation energies were obtained for the biomass-char mixtures than for the char alone, and this effect was attributed to the catalytic action of the elements contained in the biomass. Czerski et al. [20] conducted examinations on the steam gasification of tyre char with the addition of sewage sludge in ratios of 100:0, 90:10, 67:33, and 0:100 for temperatures of 800, 850, and 900 °C, and at a pressure of 1.0 MPa. The

presence of sewage sludge in the char mixture increased the rates of CO₂ and H₂ formation. The analysis of the conversion degree curves showed an increase in the reaction rate caused by the addition of sewage sludge, especially at temperatures of 800–850 °C. This is also confirmed by the juxtaposed higher values of reactivity indexes R_{0.25}, R_{0.50}, and R_{0.75} for both mixtures of tyre char with sewage sludge at the set temperature. On the other hand, the analysis of the composition of the gaseous products showed higher CO₂ and H₂ yields for the mixtures compared to the values obtained for the tyre char alone at 800 and 850 °C. The addition of sewage sludge reduced activation energy values from 227.8 kJ/mol for the tyre char to 178.3 kJ/mol for the 90:10 mixture and 138.6 kJ/mol for the 67:33 mixture.

5.10. Gasification of Oil from Waste Tyre Pyrolysis

Due to the significant presence of sulphur and nitrogen compounds, the combustion of tyre pyrolysis oil leads to increased emissions of NO_x and SO_x compared to the standard diesel fuel used in compression-ignition engines. In addition, tyre pyrolysis oil also contains high concentrations of some polycyclic aromatic hydrocarbons, such as naphthalene, fluorene, phenanthrene, and pyrene, as a result of which further use becomes difficult, as it requires extensive purification processes [173,174]. In the literature, there are few papers reporting gasification of pyrolysis oil from waste tyres. Mastral et al. [161] performed thermodynamic calculations on the gasification of tyre pyrolysis oil in both oxygen and steam atmospheres in a wide range of temperatures and pressures. Their findings indicated that the pyrolysis oil can be converted to gas. The results of the mass balance showed that the gasification of 0.61 kg of oil obtained from the pyrolysis of 1.00 kg of used tyres produces 0.16 kg of H₂, 1.96 kg of CO₂, and 0.01 kg of H₂S. In turn, Okoye et al. [162] reported that the gasification of tyre oil in a mixture of 75 vol.% N₂ and 25 vol.% O₂ led to the formation of more gaseous products, with a decrease in the yield of the solid residue. Hrabovski et al. [164] analysed the composition of the gas obtained during plasma gasification of pyrolysis tyre oil using various gasification agents (H₂O, CO₂, O₂ and CO₂ + O₂). The highest share of hydrogen (58.0%) and the lowest concentration of CO (32.0%) were obtained for steam. The use of CO₂ or a mixture of CO₂ + O₂ resulted in a significant reduction in hydrogen shares, decreasing to 27 and 19%, respectively, while increasing the CO share to 53 and 54%. In turn, plasma gasification in an oxygen atmosphere led to the lowest shares of methane and carbon dioxide in the resulting gas. Gašparovič et al. [163] studied the effect of temperature and the addition of a dolomite catalyst during examinations of steam gasification of pyrolysis oil from tyres. An increase in temperature from 600 to 800 °C resulted in an increase in hydrogen yield from 44.0 to 61.0%, with a decrease in other gas components. The authors also observed a positive effect of the presence of the dolomite catalyst, leading to a more than twofold increase in H₂ yield from 24.7 to 60.6%. There were slight increases in CO and CO₂, as well as a significant decrease in the CH₄ formed from 24.0 to 13.0%. The authors verified the possibility of catalyst regeneration; the first regeneration did not significantly affect the quality of the obtained gas. However, for the twice regenerated dolomite, a significant decrease in hydrogen formation (from 60.6 to 54.5%) was observed.

6. Conclusions

The thermochemical conversion of waste tyres is a promising method of disposal that makes it possible to obtain many valuable products while reducing emissions compared to the combustion process.

As a result of pyrolysis, the resulting gaseous, liquid, and solid products are used for energy production, chemical synthesis, and alternative fuels. The temperature and heating rate during this process are factors that determine the shares of each product and the efficiency of the entire process. The increase in temperature results in an increase in the yield of the gas and liquid fractions and a decrease in the amount of char. The use of lower heating rates results in lower proportions of the liquid fraction and an increase in solid and gaseous products, so in order to direct the process to maximize the yield of liquid

components, fast pyrolysis should be used. The particle size of the raw material mainly influences the process time. The process pressure does not play such a significant role; however, the use of a vacuum has a positive effect on the amount of oil and its composition, while the opposite effect was observed for high pressure. The use of catalysts during pyrolysis affects the rate and efficiency of the process as well as the composition of the obtained products, and their proper selection allows the desired direction of the process.

A key role in the gasification process is played by the reaction stage of the tyre char gasification reaction with the gasification agent. Tyre char has low reactivity due to its structural properties (low specific surface area and porosity) and a high C-element content. In addition, the removal of mineral matter with acids adversely affects the reactivity of this material, which indicates the catalytic effect of some inorganic compounds on gasification reactions. Process and technological conditions play a key role during the process, especially temperature, the increase of which positively affects the rate and duration of the process, the conversion degree, and efficiency. In addition, the final temperature of the process affects the yields of the various products and the composition of the resulting gas and its calorific value. Increasing the heating rate, on the other hand, results in a shift toward higher temperatures for the onset, end, and maximum rate of the reactions taking place, while the reaction rate increases. Increasing the pressure of the gasification process promotes an improvement in the conversion degree and reaction rate, increasing the yield of individual gas products, as well as the calorific value of the gas. The amount of fed gasification agent affects the composition of the gas, increasing the supply of steam, resulting in an increase in the yield of gaseous products and a decrease in the amount of the resulting liquid products and solid fraction, as well as an increase in the amount of hydrogen, carbon monoxide, and carbon dioxide obtained while reforming hydrocarbons. In addition, an increase in the concentration of the gasification agent has a positive effect on the conversion degree, and rubber waste is more reactive to steam compared to CO₂. The particle size of the raw material can affect the yields of individual products (an increase in liquid and gas occurs at the expense of solids with a decrease in particle size), as well as the composition and calorific value of the gas obtained. Due to the low reactivity of char from tyre pyrolysis in particular, it is advisable to use catalysts or co-gasification with more reactive materials to support the process. The use of catalysts makes it possible to improve the reaction rate, the conversion degree, and increase the yield of the gas fraction, while lowering the liquid fraction. Additionally, it increases the yield of individual gaseous products, especially hydrogen and carbon monoxide, and lowers the yield of hydrocarbons. Also, co-gasification with biomass materials leads to similar effects, i.e., improving the maximum conversion degree, increasing the yield of the gas fraction and CO and H₂, but lowering the reactivity indexes, reaction times and activation energies. One way to utilise the oil from waste tyre pyrolysis is through the gasification process, and using steam as the gasification agent enables the production of hydrogen-rich gas, including the use of plasma reactors.

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